



Physical Chemistry

C. G. Silcocks

Third Edition

LOW-PRICED EDITION

PHYSICAL CHEMISTRY

Some other ELBS low-priced editions

Atkins	PHYSICAL CHEMISTRY	<i>Oxford University Press</i>
Block and Holliday	MODERN PHYSICAL CHEMISTRY	<i>Butterworth</i>
Brown	A NEW GUIDE TO MODERN VALENCY THEORY	<i>Longman</i>
Cartmell and Fowles	VALENCY AND MOLECULAR STRUCTURE	<i>Butterworth</i>
Dent Glasser	CRYSTALLOGRAPHY AND ITS APPLICATIONS	<i>Van Nostrand (U.K.)</i>
Gillam and King	COLLEGE PHYSICS, Vols. I & II	<i>Macdonald & Evans</i>
Hill and Holman	CHEMISTRY IN CONTEXT	<i>Nelson</i>
Kettle	COORDINATION COMPOUNDS	<i>Nelson</i>
Kneen, Rogers and Simpson	CHEMISTRY: FACTS, PATTERNS AND PRINCIPLES	<i>Addison-Wesley</i>
Lambert	STRUCTURAL STEELWORK	<i>George Godwin</i>
Littlefield and Thorley	ATOMIC AND NUCLEAR PHYSICS	<i>Van Nostrand (U.K.)</i>
McWeeny	COULSON'S VALENCE	<i>Oxford University Press</i>
Murrell, Kettle and Tedder	THE CHEMICAL BOND	<i>John Wiley</i>
Murrell, Kettle and Tedder	VALENCE THEORY	<i>John Wiley</i>
Phillips	AN INTRODUCTION TO CRYSTALLOGRAPHY	<i>Longman</i>
Smith	SOIL MECHANICS	<i>George Godwin</i>
Templeton	ORGANIC CHEMISTRY	<i>Macdonald & Evans</i>

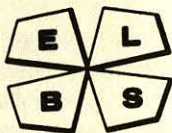
PHYSICAL CHEMISTRY

FOR ADVANCED LEVEL G.C.E.
and
TEC LEVELS I, II and III

C. G. SILCOCKS, B.Sc., Ph.D., C.Chem., F.R.S.C.

*Lately Principal Lecturer in Chemistry,
Gloucester City College of Technology*

THIRD EDITION



THE ENGLISH LANGUAGE BOOK SOCIETY
AND
MACDONALD AND EVANS
LONDON & PLYMOUTH

MACDONALD & EVANS LTD.
Estover, Plymouth PL6 7PZ

First published 1966
Second edition 1972
E.L.B.S. edition first published 1972
E.L.B.S. edition reprinted 1974
Reprinted 1976
E.L.B.S. edition reprinted 1976
Reprinted 1977
E.L.B.S. edition reprinted 1977
Third edition 1980
E.L.B.S. edition of Third edition 1980
Reprinted 1982
E.L.B.S. edition reprinted 1982

©
MACDONALD AND EVANS LIMITED
1980

ISBN: 0 7121 1697 4

This book is copyright and may not be reproduced in whole or *in part* (except for purposes of review) without the express permission of the publishers in writing.

Acc no- 15619



Printed in Great Britain by Fletcher & Son Ltd, Norwich

PREFACE TO THE FIRST EDITION

THIS book has been written primarily for students studying for the following examinations: the General Certificate of Education at Advanced level (including those taking Special papers); and National Certificate examinations in Science, for which the appropriate sections of both Basic and Elective Chemistry are covered.

The aim has been to present a logical and modern approach to the basic concepts of physical chemistry. Older ideas and obsolete experimental procedures have only been retained where they serve a useful purpose, *e.g.* by way of historical introduction, or to show the experimental basis for current theories, or (reluctantly) where they are still included in examination syllabuses.

The treatment of atomic structure and valency is based on electronic energy levels, atomic orbitals and the valence bond approach. The topics introduced at this stage include nuclear reactions, polar bonds and molecular polarity, hydrogen bonds, the metallic bond, bond lengths and bond strengths. A chapter on the kinetic theory of matter, including a discussion of the nature of intermolecular forces, precedes the properties of the states of matter and of solutions, and enables molecular interpretations of physical properties to be given.

Energy changes in chemical reactions are dealt with in terms of the first law of thermodynamics, and the thermodynamic sign convention is used. A brief outline is also given of the second law, and of the significance of entropy and free energy.

In describing the properties of electrolytes, the effect of the solvent has been emphasised. The proton-transfer theory is used to define acids and bases, and in dealing with many electrolytic equilibria. Electrolysis is illustrated by several important examples, and the nature of the electrode reactions is considered in some detail. There is also a section on corrosion.

The chapter on kinetics has been designed, not merely to state the reaction rate law, but to provide a reasoned explanation of the variation of the rate of a reaction with concentration and temperature. It therefore contains an outline of the collision theory and the activated complex theory. A separate chapter has been devoted to catalysis, and contains a large number of examples including the more important industrial catalytic processes now in use. Heterogeneous catalysis is explained in terms of adsorption.

The symbols used in this book, and the sign convention for electro-

motive force, are those recommended by the International Union of Pure and Applied Chemistry.

To ensure that students can see how mathematical equations can be applied to actual problems, there are many worked examples in the text. In addition, selected questions from General Certificate of Education Advanced level papers (G.C.E.) and Special papers (marked "S"), appear at the ends of chapters.

The author wishes to express his sincere thanks to Mr. D. M. Samuel (Gloucester Technical College) for reading the book and offering much helpful advice, and to the following boards for permission to reproduce questions from their past papers (the abbreviations given are those that appear in the text):

Oxford Delegacy of Local Examinations (*Oxford*)

University of Cambridge Local Examinations Syndicate (*Cambridge*)

Oxford and Cambridge Schools Examination Board (*O. & C.*)

University of London University Entrance and School Examinations Council (*London*)

Joint Matriculation Board (*J.M.B.*)

Welsh Joint Education Committee (*W.J.E.C.*)

C. G. Silcocks

May 1966

PREFACE TO THE THIRD EDITION

The SI units introduced in the previous edition have been extended by the use of the pascal and siemens as derived units of pressure and electric conductance respectively. The names of chemical compounds have also been revised in accordance with IUPAC rules.

Many of the examination questions (given at the end of chapters) have been replaced by more recent examples: for permission to publish these, the author is indebted to the examination boards listed in the Preface to the First Edition, and also to the following:

The Associated Examining Board (*A.E.B.*)
Southern Universities Joint Board (*S.U.J.B.*)

A new appendix containing answers to questions has also been added: these have been supplied by the author, and are not the responsibility of any examining board.

C. G. Silcocks

May 1979

CONTENTS

<i>Preface to the First Edition</i>	v
<i>Preface to the Third Edition</i>	vii
<i>List of Illustrations</i>	xi
<i>List of Tables</i>	xv
<i>Table of the Elements</i>	xvii
1. The atomic theory	1
2. Atomic structure	5
3. The chemical bond	30
4. The kinetic theory of matter	49
5. Gases	56
6. Liquids	83
7. Solids	93
8. Solutions	110
9. Properties of dilute solutions	133
10. Distillation	155
11. Thermochemistry and thermodynamics	165
12. Chemical kinetics	185
13. Chemical equilibrium	201
14. Electrolytes	220
15. Chemical cells and electrolysis	252
16. Catalysis	274
17. Colloids	286
<i>Appendix I: SI Units</i>	299
<i>Appendix II: Answers to Questions</i>	301
<i>Index</i>	307

LIST OF ILLUSTRATIONS

	PAGE
1. Apparatus for studying the deflection of cathode rays	5
2. Mass spectrograph	9
3. Energy level diagram for hydrogen	20
4. Electron shells of an atom	21
5. Electronic configuration of elements with atomic numbers 1-10	22
6. The periodic table	23
7. Representation of atoms according to Bohr	25
8. Electron orbitals for <i>s</i> electrons	27
9. Electron orbitals for <i>p</i> electrons	27
10. Formation of a hydrogen molecule	34
11. The directional nature of bonds formed with <i>p</i> orbitals	35
12. Formation of π -bonds	36
13. π -bonds in benzene	37
14. Metallic bonds	44
15. Rotation and vibration of a diatomic molecule	50
16. Forces of intermolecular attraction	52
17. Average distances between molecules in the three states of matter	53
18. Distribution of energies among gaseous molecules at different temperatures	55
19. Molecule rebounding after striking wall of container	62
20. Deviation of gases from ideal behaviour at high pressures	65
21. Non-ideal behaviour of nitrogen at different temperatures	66
22. Inward attraction on molecules near wall of vessel	67
23. Underperfect and overperfect behaviour	68
24. Work done by the expansion of a gas	69
25. Graph for obtaining the limiting density of carbon dioxide	72
26. Gas density microbalance	74
27. Victor Meyer's method for measuring the density of vapours	76
28. The vapour density method of Dumas	77
29. Pressure-volume isotherms for carbon dioxide	84
30. The disappearing meniscus method	85
31. Liquefaction of air using Joule-Thomson cooling	87
32. Inward pull on molecules at the surface of a liquid	88
33. Vapour-liquid equilibrium	89
34. Vapour pressure curve for ethanol	90
35. Determination of the boiling point of a liquid	91

36. Different forms of a sodium chloride crystal	93
37. Crystal structure of the allotropic forms of carbon	95
38. Crystal lattices of metals	96
39. The crystal structure of carbon dioxide	97
40. Ionic crystals	97
41. Heat capacities of elements	99
42. The triple point of water	101
43. Determination of melting point: capillary tube method	102
44. Determination of melting point: block method	103
45. Pressure-temperature diagram for sulphur	105
46. Pressure-temperature diagram for phosphorus	106
47. One-component phase diagram	107
48. Hydration of ions	111
49. Solubility curves for some inorganic salts in water	114
50. Partially miscible liquids: methanol-cyclohexane	117
51. Determination of the solubility of a sparingly soluble gas	124
52. Determination of the solubility of a very soluble gas	125
53. Crystal lattice of a solid solution of silver and gold	126
54. Solid solution diagram for naphthalene and 2-naphthol	126
55. Eutectic diagram for lead and antimony	127
56. Cooling curves for a eutectic system	129
57. A salt and water system	130
58. Vapour-liquid equilibrium for a solution	133
59. Curves showing the lowering of vapour pressure of a solvent due to the presence of a non-volatile solute	136
60. Boiling point elevation of a dilute solution	137
61. Depression of freezing point of a dilute solution	138
62. Differential thermometer	140
63. Cottrell's apparatus for measuring elevation of boiling point	141
64. Cooling curve showing supercooling of a solution	143
65. Apparatus for measuring freezing point depression	144
66. Osmosis	146
67. How osmosis arises from different rates of diffusion of solvent molecules through the membrane	146
68. Pfeffer's apparatus for measuring osmotic pressure	148
69. Pinner-Stabin osmometer	149
70. Vapour pressures of a mixture of two liquids	155
71. Boiling point diagram for benzene-methylbenzene	156
72. Distillation apparatus	157
73. Bubble-cap type of fractionating column	158
74. Boiling point diagram for an azeotropic system	159
75. Apparatus for steam distillation	162
76. Energy changes in reactions taking place at constant pressure and at constant volume	167
77. Calorimeter for measuring heats of reaction in solution	170
78. Method of obtaining the corrected rise in temperature	171

79. Bomb calorimeter	172
80. Energy of activation	188
81. Change of reaction velocity with time	189
82. Apparatus for measuring the rate of a gaseous reaction by means of pressure measurements	191
83. Dilatometer	191
84. Times of half change for first and second order reactions	198
85. Dissociation pressures of copper(II) sulphate hydrate systems	216
86. Conduction in an electrolyte	221
87. Bridge circuit for measuring electrolytic conductance	223
88. Variation of molar conductivity with concentration	225
89. Ionic atmosphere effect	225
90. Structural changes in indicator molecules.	240
91. pH curve for acid-base titrations	243
92. Electrical double layer	253
93. Hydrogen electrode	253
94. Measurement of electrode potential.	256
95. Current flow in a hydrogen-copper cell	258
96. The Daniell cell	260
97. Electrolysis of a solution of copper(II) chloride between platinum electrodes	261
98. Current-voltage curve for the cell shown in Fig. 97	262
99. Electrolysis of solutions between platinum electrodes	266
100. Concentration changes near the electrodes due to electrolysis	269
101. Electrolytic corrosion at the junction between two metals	271
102. Adsorption of a gas on a solid surface	281
103. Chemisorption	282
104. Dialysis	289
105. The ultramicroscope technique for "seeing" a colloidal particle	290
106. Electrophoresis	291
107. The electrical double layer round a colloidal particle.	292
108. A micelle in a soap solution	295

LIST OF TABLES

	PAGE
1. Electronegativities	40
2. Bond lengths and bond dissociation energies	42
3. Melting points and boiling points	54
4. Critical constants	85
5. Molal depression and elevation constants	139
6. Standard enthalpies of formation	174
7. Ionic conductivities at 25°C	227
8. Dissociation constants of acids and bases at 25°C	231
9. Acid-base indicators	241
10. pH changes during an acid-base titration	242
11. Solubility products	245
12. Standard electrode potentials at 25°C	257
13. Hydrogen and oxygen overpotentials	263
14. Examples of colloidal systems	287
15. Concentrations of electrolyte required to coagulate a negatively charged arsenic sulphide sol	293

TABLE OF THE ELEMENTS

<i>Element</i>	<i>Symbol</i>	<i>Atomic number</i>	<i>Relative atomic mass</i>	<i>Element</i>	<i>Symbol</i>	<i>Atomic number</i>	<i>Relative atomic mass</i>
Actinium	Ac	89	(227)	Mercury	Hg	80	200.59
Aluminium	Al	13	26.9815	Molybdenum	Mo	42	95.94
Americium	Am	95	(243)	Neodymium	Nd	60	144.24
Antimony	Sb	51	121.75	Neon	Ne	10	20.183
Argon	Ar	18	39.948	Neptunium	Np	93	237.0482
Arsenic	As	33	74.9216	Nickel	Ni	28	58.71
Astatine	At	85	(210)	Niobium	Nb	41	92.906
Barium	Ba	56	137.34	Nitrogen	N	7	14.0067
Berkelium	Bk	97	(247)	Nobelium	No	102	(254)
Beryllium	Be	4	9.0122	Osmium	Os	76	190.2
Bismuth	Bi	83	208.980	Oxygen	O	8	15.9994
Boron	B	5	10.811	Palladium	Pd	46	106.4
Bromine	Br	35	79.909	Phosphorus	P	15	30.9738
Cadmium	Cd	48	112.40	Platinum	Pt	78	195.09
Caesium	Cs	55	132.905	Plutonium	Pu	94	(242)
Calcium	Ca	20	40.08	Polonium	Po	84	(210)
Californium	Cf	98	(251)	Potassium	K	19	39.102
Carbon	C	6	12.01115	Praseodymium	Pr	59	140.907
Cerium	Ce	58	140.12	Promethium	Pm	61	(145)
Chlorine	Cl	17	35.453	Protactinium	Pa	91	231
Chromium	Cr	24	51.996	Radium	Ra	88	226.05
Cobalt	Co	27	58.9332	Radon	Rn	86	(222)
Copper	Cu	29	63.54	Rhenium	Re	75	186.2
Curium	Cm	96	(247)	Rhodium	Rh	45	102.905
Dysprosium	Dy	66	162.50	Rubidium	Rb	37	85.47
Einsteinium	Es	99	(254)	Ruthenium	Ru	44	101.07
Erbium	Er	68	167.26	Samarium	Sm	62	150.35
Europium	Eu	63	151.96	Scandium	Sc	21	44.956
Fermium	Fm	100	(253)	Selenium	Se	34	78.96
Fluorine	F	9	18.9984	Silicon	Si	14	28.086
Francium	Fr	87	(223)	Silver	Ag	47	107.870
Gadolinium	Gd	64	157.25	Sodium	Na	11	22.9898
Gallium	Ga	31	69.72	Strontium	Sr	38	87.62
Germanium	Ge	32	72.59	Sulphur	S	16	32.064
Gold	Au	79	196.967	Tantalum	Ta	73	180.948
Hafnium	Hf	72	178.49	Technetium	Tc	43	(99)
Helium	He	2	4.0026	Tellurium	Te	52	127.60
Holmium	Ho	67	164.930	Terbium	Tb	65	158.924
Hydrogen	H	1	1.00797	Thallium	Tl	81	204.37
Indium	In	49	114.82	Thorium	Th	90	232.038
Iodine	I	53	126.9044	Thulium	Tm	69	168.934
Iridium	Ir	77	192.2	Tin	Sn	50	118.69
Iron	Fe	26	55.847	Titanium	Ti	22	47.90
Krypton	Kr	36	83.80	Tungsten	W	74	183.85
Lanthanum	La	57	138.91	Uranium	U	92	238.03
Lawrencium	Lr	103	(257)	Vanadium	V	23	50.942
Lead	Pb	82	207.19	Xenon	Xe	54	131.30
Lithium	Li	3	6.939	Ytterbium	Yb	70	173.04
Lutetium	Lu	71	174.97	Yttrium	Y	39	88.905
Magnesium	Mg	12	24.312	Zinc	Zn	30	65.37
Manganese	Mn	25	54.9380	Zirconium	Zr	40	91.22
Mendelevium	Md	101	(256)				

CHAPTER 1

THE ATOMIC THEORY

1.1. The constitution of matter and the scientific method

The world around us presents an extraordinary variety of different forms of matter, but we now know a great deal about the way in which matter is constituted and how it will behave under different conditions. This is the result of applying the *scientific method*. Since a clear grasp of the scientific method will be of help in understanding physical chemistry, the steps in this line of approach will be described.

(i) Experiments are carried out. They may be concerned with studying chemical reactions, measuring physical properties, etc., according to the nature of the problem.

(ii) The experimental results are examined to see whether there is any general statement or mathematical expression which is true for all of them: if so, it is stated as a *law*.

(iii) Finally, it may be possible to suggest a *theory* which accounts for the observed facts.

The following example illustrates this sequence. The volume of a gas is found to vary with changes in temperature and pressure: measurements show that the pressure, volume and temperature are related by simple mathematical expressions (the gas laws). From these and certain other facts a theory of gases was proposed (the kinetic theory), which was found to be in agreement with the gas laws.

It is important to realise that laws and theories only relate to the facts *as they are known at the time*. As further, and possibly more accurate, experiments are performed it may be found that there are exceptions to the laws, or fresh facts that do not agree with the theories. The result is that theories are not necessarily permanent and may have to be modified, or even discarded, in the course of time.

The first four chapters of this book will be concerned with the basic chemical units (atoms and molecules) from which matter is built up, and will show how the present theories of the structure of these units have been arrived at mainly from a study of physical properties.

1.2. The elements

The idea that all substances are made up of a limited number of simple constituents, or *elements*, was first put forward by Robert Boyle in 1661, in the early days of true experimental chemistry. An element may be defined as *a substance that cannot further be divided into other chemical constituents*. A total of 103 chemical elements is now known,

but not all of these occur in nature and practically all naturally occurring matter is made up from combinations of only 88 different elements. The number of compounds that can be formed from even this comparatively small number of elements is very large, and over a million different chemical substances are known today.

1.3. The atomic theory

Up to the middle of the eighteenth century, experimental chemistry was largely qualitative and little importance was attached to the masses of reacting substances. The first real quantitative work was carried out during the second half of that century, and certain facts were established about the amounts of different elements that would combine together. The results of a large number of experiments are summarised in what are called the *laws of chemical combination*.

The *law of conservation of mass* states that *there is no change in the total mass of a system as a result of a chemical change* (the term *system* includes all the substances taking part in, or produced by, the reaction). This law is, in fact, assumed to hold whenever any quantitative chemical experiment is carried out, and it is justified by the fact that no change in mass has ever been detected as a result of a chemical reaction. The law does not apply to certain *nuclear* reactions (§ 2.6), where a small loss of mass may occur, but even then the decrease in mass is exactly balanced by the liberation of an equivalent amount of energy. This exception does not affect the application of the law to normal laboratory reactions, in which nuclear changes do not occur.

The *law of constant composition* states that *any given chemical compound always contains the same elements in the same proportions by mass*. The truth of this law is assumed every time the chemical formula of a compound is written. When it was first stated, the law was disputed by Berthollet, who claimed that certain metal oxides and sulphides had variable compositions. We now know that this *is* the case, and such compounds are called "Berthollides" or non-stoichiometric compounds. There are also very small variations in compounds containing certain elements (e.g. sulphur) whose relative atomic masses are subject to slight natural variations (§ 2.7).

The *law of multiple proportions* states that *when two elements combine to form more than one compound, the masses of one element combining with a fixed mass of the other are in simple multiple proportion*. Part of the evidence on which this law was based was the composition of the oxides of nitrogen: in the five different oxides that can be formed, the masses of oxygen combining with a constant mass of nitrogen are exactly in the ratio 1:2:3:4:5.

These last two laws show that elements combine only in multiples of certain basic mass units, and this fact led to the proposition advanced by John Dalton in 1808 of the *atomic theory*, the main points of which may be stated as follows:

(a) Matter is composed of a large number of very small particles, or *atoms*.

(b) It is impossible, by chemical means, to destroy or divide atoms, or to create new ones.

(c) All atoms of the same element are identical, and therefore are of equal mass and exhibit the same properties.

(d) Atoms of different elements differ in both mass and properties.

(e) Compounds are formed by the combination of small numbers of atoms of the different elements concerned.

It follows from this that an atom may be defined as the smallest particle of matter that can take part in a chemical change.

Once it is accepted that elements are composed of small and indestructible atoms of definite and constant mass, the laws of chemical combination are readily explained, since combination can only occur between whole numbers of atoms and the combining masses must therefore be in certain definite proportions. The fact that atoms are not destroyed in the process means that the total mass must remain constant, in agreement with the law of constant composition.

The law of multiple proportions was put forward by Dalton at the same time as, and in support of, his atomic theory. Soon afterwards, fresh evidence was provided by the discovery of the *law of reciprocal proportions*, which showed that, *if an element A can combine with either of two elements B and C, then the masses of B and C which will combine separately with a fixed mass of A are either the same as, or in simple ratio to, the masses of B and C which will themselves combine.*

It should be noted that the above laws were based on the compositions of simple compounds, such as metal oxides, the oxides of nitrogen, and organic compounds containing small numbers of atoms (methane and ethane). In compounds where larger numbers of atoms are united (e.g. the higher hydrocarbons) the ratios of the combining masses of the two elements would not be given by such simple numbers.

1.4. Relative atomic mass

All quantitative chemical work is based on the masses of substances involved in a particular reaction, and it is evident from the atomic theory that these masses depend on the actual masses of the various atoms concerned. It will be seen later (§ 2.5) that the atoms of a particular element do not always have the same mass, as Dalton thought. However, owing to natural mixing processes, the *average* mass is nearly always the same, so that no appreciable error arises if this average value is used as though it were the actual mass of each atom. Further, since we are only interested in the *relative* amounts of different atoms which combine together, it is not necessary for us to know the actual masses of the atoms—only their masses relative to one another. This must be found by reference to a fixed standard.

It is convenient to choose the standard so that the relative mass of the atom of the lightest element (hydrogen) is about 1. Dalton used hydrogen as the standard ($H = 1$). Later, oxygen ($O = 16$) replaced hydrogen and was used until quite recently. But it was found to be unsatisfactory because of a slight natural variation in the average mass of oxygen atoms, and because physicists (who are interested in the relative masses of individual atoms) had to use a different standard. The present standard, which was adopted internationally in 1961, is based on the mass of a single type of atom (one of the isotopes of carbon, ^{12}C ; this term is explained in § 2.5), which is given the relative mass of exactly 12 ($^{12}\text{C} = 12$). The *relative atomic mass* (formerly called the *atomic weight*) of an element is the mass of an atom of that element relative to this standard. Thus the relative atomic mass of carbon is 12.01115, because the naturally occurring element contains a small proportion of a slightly heavier atom mixed with the standard isotope.

After the publication of the atomic theory, Dalton and other chemists (notably Berzelius) made the first attempts towards establishing a list of relative atomic masses of the elements. The data on which their calculations were based were the combining masses of elements, but in order to convert these into relative atomic masses it was necessary to make assumptions about the numbers of atoms of each element in the compounds that were formed. Thus, Dalton knew that one part of hydrogen combined with eight parts of oxygen to form water, but he had no means of knowing the chemical formula of water and so he assumed that one atom of hydrogen combined with one atom of oxygen, thus giving the relative atomic mass of oxygen as 8 (taking $H = 1$).

The problem was eventually solved by studying not only the chemical properties, but also the physical properties of elements and their compounds (e.g. heat capacity, crystal structure, and density in the gaseous state). The way in which these properties can be used to fix the relative atomic masses will be explained in later chapters.

CHAPTER 2

ATOMIC STRUCTURE

2.1. Electrons and protons

Dalton's assumption that atoms were indivisible was soon shown to be incorrect, and this was first demonstrated by observations on the way in which gases can conduct electricity. When a gas at very low pressure is sealed up in a glass tube, the application of a high voltage between two electrodes in the gas causes a current to flow. During experiments of this kind Sir William Crookes noticed that a stream of rays travelled away from the negative electrode, or cathode (hence they are named *cathode rays*), and that when the rays struck the tube the glass became luminous. Sir J. J. Thomson investigated the nature of cathode rays with an apparatus similar to that shown in Fig. 1: the rays pass through a slit in the positive electrode, or anode, and produce a luminous spot where they strike the end of the tube. Thomson showed that when an electric field was applied, by connecting the plates marked *E* in Fig. 1 to a high voltage source, the rays were deflected. This proved that the rays were actually a stream of charged particles. A magnetic field, produced by an electromagnet outside the tube, also caused a deflection. Since the particles travel from the cathode towards the anode, they must carry a negative charge. By measuring the extent of the deflections caused by the electrical and magnetic fields, Thomson was able to calculate the ratio of the charge

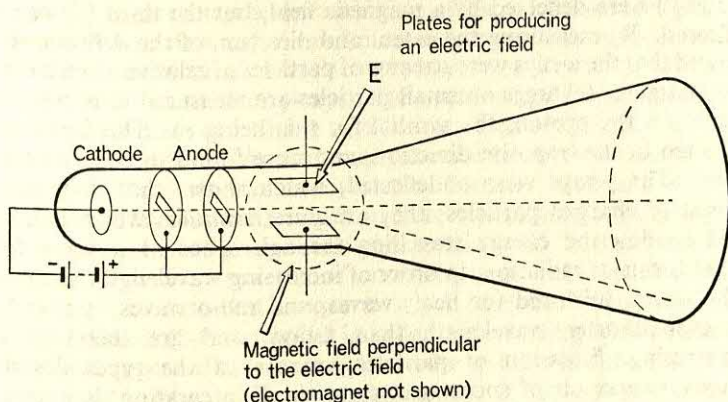


Fig. 1. Apparatus for studying the deflection of cathode rays by electric and magnetic fields

on the particles to their mass, and found that it was constant no matter what gas was used in the tube or from what material the cathode was made. He concluded that the particles were universal constituents of matter, and named them *electrons*. The charge carried by an electron was measured later, by Millikan, thus enabling the mass to be calculated. The electron is a very light particle, having a mass $\frac{1}{1838}$ that of a hydrogen atom.

In further experiments with electrical discharges through gases, Goldstein discovered that there were also rays travelling towards the cathode. If the cathode was perforated, they passed through the holes and could be seen on the far side as luminous streamers. These rays are also deflected by electric and magnetic fields, and since they move towards the cathode they evidently consist of streams of positively charged particles: they are therefore called *positive rays*. Measurements showed that the charge and mass of these particles varied, but that the lightest of them (obtained when hydrogen was present in the tube) had the same mass as a hydrogen atom, and a charge equal in magnitude (but of opposite sign) to that of the electron. This particle is evidently a hydrogen atom that has lost an electron, and we now know that the *proton*, as the particle is called, is also a fundamental constituent of all matter.

2.2. Radioactivity

The atoms of some elements, for example uranium and radium, are unstable and spontaneously disintegrate with the evolution of invisible rays. The existence of these rays was discovered in 1896 by Becquerel, who noticed that uranium salts caused photographic plates to blacken even when wrapped in the usual light-proof paper. Rutherford investigated the nature of these rays by passing them through magnetic and electric fields, and showed that there were three different types: two (α and β) were deflected by a magnetic field, but the third (γ) was not deflected. By measuring the extent and direction of the deflections, he showed that the α -rays were streams of particles of relative atomic mass 4 and charge $2e$ (charges on small particles are measured in terms of the charge on the proton, the symbol for this being e). The β -rays were deflected in the opposite direction, and were found to consist of electrons. The γ -rays were undeflected, which shows that they do not consist of charged particles: they are pure *radiation*, which is a term used to describe energy travelling through space as a wave form. Other forms of radiation, in order of increasing wavelength, are x-rays, light waves, infra-red (or heat) waves, and radio waves. γ -rays have an even shorter wavelength than x-rays, and are therefore very penetrating. Emission of particles or rays of the types described above, as a result of spontaneous atomic disintegration, is known as *radioactivity*.

The α -particles, with a mass four times that of a hydrogen atom,

are much heavier than β -particles (electrons); they are also emitted at high velocity. A radioactive substance (such as radium) is therefore a source of fast and heavy particles, and can be used as a "gun" to shoot these particles at a suitable target. If a thin metal foil is bombarded with α -particles by this means, it is found that most of the particles pass straight through, while a small proportion are deflected at considerable angles. From the result of this experiment, Rutherford deduced that matter is far less dense than might be imagined, since the particles that pass through the foil without deflection cannot have encountered in their path any appreciable concentration of mass (or of positive charge, since this would repel the positively charged particles). He therefore suggested that the mass of an atom is largely concentrated in a very small *nucleus*, which is positively charged; and that the rest of the space occupied by the atom contains the electrons, whose mass is only a very small proportion of the total mass of the atom. Since atoms have no electrical charge, the positive charge on the nucleus must exactly balance the negative charge of the electrons. The penetrating power of α -particles shows that they must themselves be small in size: they are, in fact, the nuclei of helium atoms. As they have a positive charge of $2e$ it follows that the helium atom must contain two electrons. It has already been seen that the hydrogen atom contains one proton and one electron, so that the nucleus of the hydrogen atom is a single proton. In larger atoms the nucleus contains a number of protons equal to the number of electrons in each case.

Some idea of the minute size of the atomic nucleus may be gathered by the fact that it occupies only about 10^{-12} of the total volume of the atom.

2.3. Atomic number

During experiments with cathode rays, Röntgen discovered that when the rays fell upon matter a new radiation of very short wavelength was produced. These new radiations he named x-rays. In terms of wavelength they lie between ultra-violet and γ -rays, and they are penetrating, but to a lesser extent than γ -rays. The usual way of producing x-rays is to direct a stream of cathode rays on to a metal target, from which the x-rays are emitted. An important connection between x-rays and the chemical elements was discovered by Moseley, who showed that when cathode rays fall on a target made of one particular element, the x-rays produced have frequencies characteristic of that element. By arranging the elements in order of increasing frequency of their characteristic x-rays, he arrived at a sequence which started with hydrogen and proceeded almost (but not quite) in order of increasing relative atomic mass. There appeared to be some gaps in the series, which he concluded to correspond to (then) undiscovered elements. If the elements are now numbered in this order, we obtain the *atomic numbers* (or *proton numbers*) running from hydrogen (1) to uranium (92) for the naturally occurring

elements. A similar arrangement of the elements had already been made on the basis of their relative atomic masses (see § 2.8) but there were certain anomalies in that scheme which disappeared when Moseley's method of arrangement was used.

The atomic number evidently has a more fundamental significance than the relative atomic mass. It is, in fact, directly connected with the structure of the atom, for further work on the scattering of α -particles by atomic nuclei showed that the positive charge on a nucleus is the same as the atomic number. From this the very important conclusion can be drawn that the atomic number of an element is equal to the number of electrons in each atom.

2.4. The neutron

The atom has so far been shown to contain two types of particle: protons (relative mass 1, charge e), and electrons (mass very small, charge $-e$). The number of each particle in any particular atom is equal to the atomic number. Let us now see how this compares with the relative atomic mass. The first two atoms will serve the purpose, namely hydrogen and helium, with atomic numbers 1 and 2. The relative atomic mass of hydrogen is very close to 1, which is to be expected if the nucleus of a hydrogen atom consists of a single proton. With helium, however, the relative atomic mass is 4, whereas the nucleus can only contain two protons (relative mass = 2). The additional mass must be made up of some uncharged particles. Rutherford suggested that there might be a particle with the same mass as a proton, but with no charge, and he named this particle the *neutron*. It was not until some time later that the existence of neutrons was actually demonstrated by Chadwick.

Apart from protons and neutrons, it is now known that there are other particles in the nucleus, some of which have only recently been discovered. These particles have considerable bearing on the problem of how the various pieces of the nucleus are held together, but in studying the structure of the atom in relation to its chemical properties we may disregard them and consider atoms as made up of protons, neutrons and electrons.

Consider the first four elements, *i.e.* those with atomic numbers 1-4. These all have relative atomic masses that are very nearly whole numbers, and we can now work out the constitution of their atoms as follows:

Element	H	He	Li	Be
Atomic number	1	2	3	4
Relative atomic mass	1	4	7	9
Nucleus {				
Number of protons	1	2	3	4
Number of neutrons	0	2	4	5
Number of electrons	1	2	3	4

The relative atomic masses given above have been taken to the nearest

whole number. Relative atomic masses are never exactly whole numbers, although in many cases they are close to it. There are several reasons for this:

- (a) The relative masses of the proton and neutron are both slightly greater than 1.
- (b) When a nucleus is formed, a small change in mass occurs.
- (c) The atoms of one particular element may not all have the same mass, in which case the relative atomic mass is an average value.

2.5. Isotopes

The technique developed for investigating positive rays, by studying the deflection of the particles in magnetic and electric fields, can be usefully applied to separating atoms of different mass. Working along these lines, Aston developed the first *mass spectrograph*, an instrument which sorts out positive particles according to their various masses and produces a photograph of the result. Fig. 2 illustrates the principles of a more recent type of mass spectrograph. Atoms of the element, which

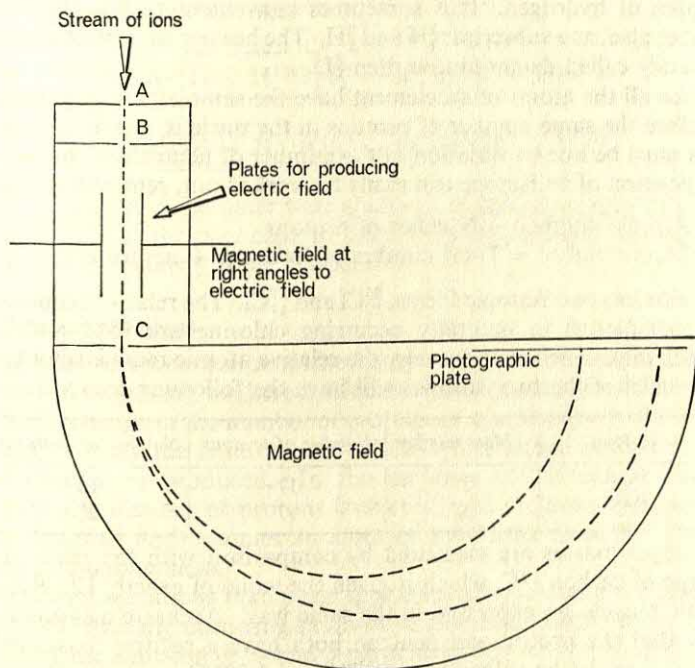


Fig. 2. Diagram of a mass spectrograph

must be vaporised if not already a gas, are bombarded with a stream of electrons. The positive ions produced are restricted to a narrow beam by passing through the two slits A and B, and then subjected to opposing electric and magnetic fields. Slit C selects only those ions that pass

through the fields without deviation; it can be shown that these must all have the same velocity, whatever their mass. The ions finally pass through another magnetic field, which deflects them in circular paths according to their mass. A photographic plate placed in their path records the position at which the paths of different ions finish, and from this the different masses of the particles can be very accurately calculated.

When elements are examined with the mass spectrograph, it is found that the majority of them contain atoms of different mass. Hydrogen, for example, consists of a mixture of atoms of relative mass 1 and 2 respectively: there is only a small proportion of the latter, so that the relative atomic mass (which is the average value) is approximately 1. All hydrogen atoms, however, have the same chemical properties. Atoms of the same element—*i.e.* having the same atomic number and chemical properties—but differing in mass are called *isotopes*. In order to distinguish between the different isotopes of an element, the *mass number* (equal to the total number of protons and neutrons) is written as a superscript before the symbol of the element, *e.g.* ^1H and ^2H for the isotopes of hydrogen. It is sometimes convenient to add the atomic number also, as a subscript: ^1_1H and ^2_1H . The heavier isotope of hydrogen is usually called deuterium, written ^2_1D .

Since all the atoms of an element have the same atomic number and therefore the same number of protons in the nucleus, the differences in mass must be due to variation in the number of neutrons. The nuclear composition of an isotope can easily be worked out, remembering that:

Atomic number = Number of protons

Mass number = Total number of (protons + neutrons)

Chlorine has two isotopic forms, $^{35}_{17}\text{Cl}$ and $^{37}_{17}\text{Cl}$. The relative proportions (or *abundances*) in naturally occurring chlorine are 75% and 25% respectively, which explains why the relative atomic mass is about 35.5. The nuclei of the two isotopes will have the following composition:

Isotope	Mass number	Number of protons	Number of neutrons
$^{35}_{17}\text{Cl}$	35	17	18
$^{37}_{17}\text{Cl}$	37	17	20

Isotopic masses are measured by comparison with the mass of the isotope of carbon ^{12}C , which is given the value of exactly 12. Relative atomic masses are expressed in the same way. Accurate measurements show that the proton and neutron both have a relative mass slightly greater than 1 (the values are 1.00726 and 1.00861 respectively), which means that the ^{12}C isotope has a mass slightly less than would be expected:

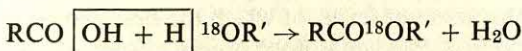
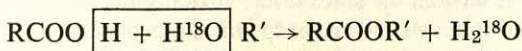
$^{12}_6\text{C}$ atom contains 6 protons, 6 neutrons, 6 electrons.

$$6 \times 1.00726 + 6 \times 1.00861 + 6 \times 0.00055 = 12.09852$$

$$\text{Relative atomic mass} = 12.00000$$

The decrease in mass, or *mass defect* as it is called, is due to the very strong forces which bind the protons and neutrons together in the nucleus. If a carbon nucleus were built up from its separate constituents, a very large amount of energy would be released and this would be exactly balanced by a corresponding decrease in mass. This is in accordance with the principle, first stated by Einstein, that mass may be converted into energy under certain conditions, the amount of energy E produced by a decrease in mass of m being given by $E = mc^2$, c being the velocity of light.

Isotopes have been of great use in elucidating the mechanisms of chemical reactions. The procedure is to replace selected atoms by an isotope of the same element but of different mass, and analyse the products of the reaction to find out where the atoms that have been "labelled" in this way occur. An example is the esterification reaction between a carboxylic acid and an alcohol, which has been studied by using alcohols containing the ^{18}O isotope (naturally occurring oxygen consists almost entirely of the ^{16}O isotope). There are two possible paths for the reaction to take:



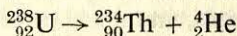
When the ester and the water were analysed, using a mass spectrometer, it was found that the ester contained the ^{18}O isotope, thus showing that the second mechanism is the correct one.

2.6. Nuclear reactions

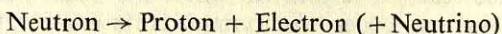
Chemical reactions are concerned only with the electrons in atoms, the nucleus remaining unaltered. Nuclear reactions, on the other hand, result in a change in the number of protons or neutrons (or both) in the nucleus. If only the neutrons are affected, a different isotope of the same element is produced. In the majority of nuclear reactions, however, the number of protons is altered, and the atom changes its atomic number and becomes an atom of a different element. This is known as *transmutation*.

Some transmutations take place spontaneously, owing to the disintegration of naturally occurring radioactive elements. Such changes are caused by the emission of α - and β -particles (§ 2.2) from the nucleus of the atoms, and in many cases the rate at which it occurs (the rate of decay) is extremely slow. This explains why radioactive substances still exist in nature. The decay rate is expressed in terms of the half-life, *i.e.* the time taken for half the original amount of material to decay. Unlike chemical reactions, the rate of a nuclear reaction cannot be increased by any means; increasing the temperature, for example, has no effect.

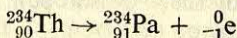
Natural uranium consists of three radioactive isotopes, all with very long half-lives (the longest is 4,500,000,000 years). When the most abundant isotope (^{238}U) decays, it emits an α -particle (helium nucleus, ^4_2He) and the atomic number is reduced by two so that the atom becomes an isotope of thorium:



The thorium isotope is also radioactive, with a half-life of 24 days, and emits a β -particle (electron) from the nucleus. There are no electrons in atomic nuclei, and it is thought that β -particles are produced by the conversion of a neutron into a proton and an electron (it is necessary to the theory that another particle called a neutrino, of very small mass and uncharged, should be produced at the same time):



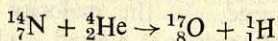
This means that the nuclear charge, and therefore the atomic number, are increased by one, and an isotope of protactinium is formed:



The electron is written $^0_{-1}\text{e}$ since it has virtually no mass and a charge of -1 (measured in terms of the charge on the proton).

Radioactive decay proceeds in stages until finally a stable isotope is formed. In the uranium series, of which the first two stages are shown above, the end product is an isotope of lead. Some of the intermediate products have long half-lives, for example radium occurs in the above series and has a half-life of 1,600 years. This explains why radium is found in measurable quantities in uranium ore, from which it was first isolated by Mme Curie.

Nuclear reactions can also be made to take place by bombarding atoms with protons, α -particles, neutrons and other small particles. The first reaction of this type was observed by Rutherford in 1919, when he found that α -particles from a radioactive source would interact with nitrogen atoms. We now know that the nitrogen had been converted into an isotope of oxygen by the following reaction:



What Rutherford actually observed at the time was that protons (^1_1H) were produced.

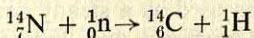
In reactions of this type the bombarding particle enters the nucleus of the atom, but the resulting *compound nucleus* is unstable and expels another type of particle (such as the proton in the above example). When the bombarding particles are positively charged, e.g. protons and α -particles, there is strong repulsion by the positively charged nucleus, and in most cases the particle cannot enter the nucleus unless it has a very high energy. Many artificial transmutations have only been made possible by accelerating charged particles to a high velocity by passing them through strong electric fields. One type of instrument in which this

can be done is the *cyclotron*, in which a magnetic field causes the particles to move in a spiral path of increasing radius as their speed is increased. When neutrons are used as the bombarding particle there is no electrical repulsion, since the neutron has no charge, and high energy is not required. Atomic reactors have been very useful as sources of neutrons.

Artificial transmutations have been used to make elements that have no stable isotopes and therefore are not found in nature. These include the elements technetium and promethium, for which gaps had to be left in the periodic table at atomic numbers 43 and 61; and the elements beyond uranium (92), which is the last naturally occurring element. These new *transuranic elements* are all radioactive, and in most cases the quantities obtained have been extremely small: the study of their properties has led to the development of new techniques of "ultramicro-chemistry."

Another important application of transmutation reactions is for the production of radioactive isotopes of stable elements. These are often used as "tracers" by introducing them into chemical compounds in place of the normal atoms. Their presence can readily be detected by virtue of the radiation they emit, so that they can be followed through the course of a chemical or physical change. Some of the many applications of radioactive tracers are: investigation of the mechanisms of chemical reactions; following the path taken by certain elements in the human body; measuring the solubility of very slightly soluble materials; and in chemical analysis.

A widely used tracer is radiocarbon, which is the isotope ^{14}C . This can be produced by bombarding ^{14}N (the most common isotope of nitrogen) with neutrons:



Radiocarbon is present in very small amounts in the carbon dioxide in the earth's atmosphere, being formed by the continual bombardment with cosmic rays in the upper atmosphere. This forms the basis of the radiocarbon dating method for finding the age of long-dead plant and animal remains. Living things absorb the radiocarbon while they are alive, and after death this starts to decay with a half-life of 5,600 years. By measuring the proportion of carbon present as the radioactive isotope it is possible to calculate the age of the remains over a span of tens of thousands of years.

In 1938 a new type of nuclear reaction was discovered by Hahn and Strassmann. They found that when uranium atoms were bombarded with neutrons, one of the products was barium, which has a mass roughly half that of uranium. It was soon realised that the uranium nucleus, after absorbing the neutron, must have split into two parts of almost equal size. This process is called *nuclear fission*. An important characteristic of fission reactions is that when a heavy nucleus is split a very large amount of energy is liberated: it is calculated that fission

of the uranium isotope ^{235}U releases energy equivalent to the combustion of two million times its weight of coal. This is enormously greater than the energy liberated by any chemical reaction, and shows how much stronger the binding forces are in nuclei compared with chemical bonds. In accordance with the mass-energy relation (p. 11), the total mass of the fission products is appreciably less than the mass of the original atom (plus the neutron), the difference being exactly equivalent to the amount of energy emitted.

Heavy atoms undergoing fission can split in many different ways, but the products are always within a certain size range (for ^{235}U , they have masses between 70 and 160). This is because the stability of nuclei depends on their size, both heavy and light nuclei being less stable than those of intermediate mass. The fission products represent a state of greater stability, and therefore lower energy, than the original atom, so that energy is released. The same result can be achieved if two light atoms are caused to fuse together (*nuclear fusion*) to form a heavier one. There are thus two ways in which large amounts of energy could be produced by means of nuclear reactions, at any rate in theory: fission and fusion.

Some fission reactions have a further important characteristic: for each nucleus that splits, two or more neutrons are emitted. Each neutron is capable of causing a fresh fission reaction, and—providing not too many of the neutrons escape without being usefully employed in this way—the reaction can keep itself going. If more than one neutron from each fission starts a fresh reaction, the whole process will go at a continually increasing speed and an explosion may result. This is what happens in the atomic bomb.

When nuclear fission is used as a steady source of energy, e.g. for generating electricity or driving a ship, the rate of fission has to be carefully controlled. This is done in a *nuclear reactor*, where the fuel (i.e. the fissionable material) is packed between blocks of graphite, which act as a moderator by slowing down the neutrons. The rate at which energy is produced is controlled by inserting or withdrawing rods containing a neutron absorber, such as cadmium. The energy that is released causes the temperature of the reactor to rise, and the heat is carried away, usually by carbon dioxide circulating through the reactor, to a boiler which raises steam to drive a turbine.

Nuclear fusion reactions are not self-sustaining at ordinary temperatures, but they become so if heated to an extremely high temperature. Such reactions take place in stars, but it is difficult to obtain the necessary conditions on earth. An example of fusion is the reaction between two atoms of deuterium:



This would need a temperature of about $100,000,000^\circ\text{C}$. Fusion has been achieved in the hydrogen bomb, using the high temperature

produced by an atomic bomb, but the problem of producing controlled energy from such reactions has not yet been solved.

2.7. Determination of relative atomic masses

The table on p. xvii shows the present accepted values for the relative atomic masses of the elements. They were decided upon by the International Union of Pure and Applied Chemistry after considering the best figures available, and are revised every few years. The following methods are used for determining relative atomic masses:

- (a) The mass spectrometer.
- (b) Chemical methods.
- (c) Measurement of gas densities.

Of these the mass spectrometer gives the highest accuracy, and more than half the relative atomic masses given in the table have been determined in this way.

Mass spectrometer method

This instrument is similar in principle to the mass spectrograph (p. 9), the atoms being first ionised and then passed through electric and magnetic fields so that the different isotopes are separated. At the end of their path, the ions pass through narrow slits on to collector plates, and the current flowing from the plate is a measure of the number of ions arriving there. By varying the field strength, isotopes of different mass can be focused on the slit, and so the isotopic abundances (*i.e.* the relative proportions of the different isotopes) can be found. The mass of each isotope can also be calculated from the field strength required to produce a certain deflection. From these figures the relative atomic mass can be calculated; for example, hydrogen is found to have the following composition:

<i>Isotope</i>	<i>Isotopic mass</i>	<i>Abundance</i>
^1H	1.007826	99.985%
^2H	2.014102	0.015%

so that the relative atomic mass, which is the average mass of the two isotopes in the above proportions, is given by:

$$\begin{aligned}\text{Relative atomic mass} &= 1.007826 \times 0.99985 + 2.014102 \times 0.00015 \\ &= 1.00797\end{aligned}$$

The high accuracy attainable by this method can be seen from the above example: it is about 1 part in 100,000.

Chemical methods

These are based on determinations of the mass of an element which will combine with a known mass of another element the relative atomic mass of which is already known. Combining masses depend on two

factors: (a) the relative atomic masses of the two elements, and (b) the number of atoms of each element that combine together. The latter depends on the combining power of the atoms, or *valence*. The *valency* is defined as *the number of atoms of hydrogen which one atom of the element will combine with or replace*. The valency must therefore always be a whole number, but most elements have more than one valency.

Combining masses of elements may be expressed as *equivalent masses*, i.e. *the mass in grams which will combine with 8 grams of oxygen* (more accurately, 7.9997 grams), *or the equivalent mass of any other element or compound*. This means that the equivalent mass is equal to the relative atomic mass divided by the valency, so that numerically

$$\text{Relative atomic mass} = \text{Equivalent mass} \times \text{Valency}$$

In early chemical determinations of relative atomic mass, elements were often combined directly with oxygen to form the oxide. The reverse process, i.e. reduction of the oxide with hydrogen, was also used in the case of metallic elements. From experiments such as these the equivalent masses of many elements were found, but difficulty was experienced in converting them into relative atomic masses because the valencies of the elements were not known with certainty. Fortunately, several solutions of the problem were found: a relationship was discovered between the heat capacities of solid elements and their relative atomic masses (Dulong and Petit's Law, § 7.5); information about the valencies of certain elements was deduced from the similarity between the crystalline form of their salts and those of other elements (isomorphism, § 7.4); and the periodic classification of the elements (§ 2.8) showed where an element was out of its correct place owing to an incorrect relative atomic mass. This is now only of historical interest, since the relative atomic masses of all the elements are known and the aim is only to measure them more accurately.

Chemical determinations suffer from the disadvantage that they are not capable of achieving the very high accuracy demanded by modern measurements; they have therefore been largely superseded by mass spectrometry. The only method in recent use is one devised by Stas in 1860, in which the chloride of an element is analysed to find the mass of the element that has combined with the equivalent mass of chlorine. This is done by adding a slight excess of silver nitrate solution to a solution of the chloride, then filtering off the precipitate of silver chloride and weighing it. To obtain the highest possible accuracy, many precautions have to be taken, such as purifying the chloride of the element by several recrystallisations, washing the precipitate free from other substances carried down with it, removing the last traces of water from the precipitate (ordinary drying methods do not accomplish this), and taking into account the small amount of silver chloride left in solution (which can be ignored in gravimetric work of ordinary accuracy).

Gas density method

The relative molecular mass of a gaseous substance can be found with high accuracy from measurements of its density, using the method of *limiting density* which is described in detail in § 5.8. The relative atomic mass of a gaseous element is equal to the relative molecular mass divided by the *atomicity*, i.e. the number of atoms in the molecule, which is a whole number. The method has been very useful for determining the relative atomic masses of the noble gases (for which chemical methods cannot be used), particularly since measurements can be made with very small quantities of material. The relative atomic mass of neon is still based on gas density measurements. Elements which form gaseous compounds can also be studied; for example, by determining the relative molecular mass of CO_2 and subtracting twice the relative atomic mass of oxygen, the relative atomic mass of carbon can be found. Mass spectrometer determinations have now replaced most of those made by this method.

The accuracy with which measurements can now be made has shown that the relative atomic masses of some elements are liable to slight variation, owing to differences in the proportions of the isotopes. For boron and sulphur the natural variation is ± 0.003 , for silicon ± 0.001 , while hydrogen, oxygen and carbon have smaller variations. In ordinary quantitative chemical work these variations can be disregarded because they are outside the limits of accuracy of the experiment.

2.8. The periodic table

When the elements are arranged in order of increasing atomic number, certain chemical (and physical) properties are found to repeat themselves in elements separated by definite intervals or periods; hence the name *periodic table* for such an arrangement. The first comprehensive table of this sort was drawn up by Mendeléef in 1869, at a time when atomic numbers were unknown. He used relative atomic masses to obtain the sequence, and soon found that some elements were wrongly placed and had to be transposed. He also had to leave gaps in some places in order to preserve the correct grouping according to the chemical properties, and deduced—correctly—that the gaps marked the position of hitherto undiscovered elements.

If the first eighteen elements (atomic numbers 1–18) are set out in the periodic manner, they appear as follows:

						¹ H	² He
³ Li	⁴ Be	⁵ B	⁶ C	⁷ N	⁸ O	⁹ F	¹⁰ Ne
¹¹ Na	¹² Mg	¹³ Al	¹⁴ Si	¹⁵ P	¹⁶ S	¹⁷ Cl	¹⁸ Ar

Hydrogen is in a category of its own, but the others give us the first members of eight *groups* of elements each displaying characteristic chemical and physical properties, starting with the alkali metals (first

members, lithium and sodium) and ending with the noble gases (helium, neon and argon). Reading across the table, we have what are called the *periods*, the first consisting of two elements and the next two periods having eight elements in each.

The table shows that there is a direct connection between the atomic number of an element and its chemical properties, and we know that the atomic number is equal to the number of electrons in the atom. It is reasonable to deduce that the chemical properties of an atom are determined by the number of electrons. In making this deduction we are assuming that chemical reactions involve only the electrons, and not the nuclei: during a chemical reaction the nuclei of the atoms concerned do not approach each other closely enough for interaction to occur.

The eighth group (the noble gases) is unique in that its members are much less reactive, chemically, than other elements. Considering the first three members of this group, it would therefore appear that groupings of 2, 10 or 18 electrons in an atom constitute a stable arrangement which shows little tendency to react with the electron systems of other atoms. Lithium and sodium, on the other hand, both have one electron in excess of one of these stable groupings, and both are chemically reactive and have similar chemical properties. Beryllium and magnesium have two electrons in excess and resemble each other in chemical properties, while differing from other groups.

So far, the relation between chemical properties and the number of electrons seems to be a fairly simple one. However, in the next period (starting with atomic number 19) the position becomes more complicated. Before going on, we must find out more about how the electrons are arranged, in other words, the electronic structure of the atom. A good deal of our knowledge of this is based on the evidence of spectra.

2.9. Atomic spectra

Anyone who has carried out qualitative inorganic analysis will know that certain elements, when heated in a flame, give characteristic colours. If the light from such a flame is passed through a spectroscope (an instrument in which the light beam is split, by means of a prism, into its individual wavelengths), the *spectrum* produced is seen to consist of a number of narrow coloured lines. This is known as a line spectrum, and each line represents a sharply defined wavelength. Radiation is a form of energy, and the spectrum is produced by the atoms absorbing energy when heated in the flame and then emitting this energy (or part of it) in the form of radiation. The question now arises: why does an atom only emit radiation of certain definite wavelengths, characteristic of that particular type of atom?

Part of the answer to this question was provided by the *quantum theory* put forward by Planck and later developed by Einstein: the theory states that a body cannot absorb or emit energy continuously, but only intermittently in small packets or *quanta*, the energy (E) of a

quantum being directly related to the frequency of the radiation (ν) by the equation

$$E = h\nu$$

where h is a universal constant known as the Planck constant. One consequence of this theory is that radiation must consist of a stream of small energy packets (once graphically described as "light darts"); however, a beam of radiation contains such a large number of these that it behaves in many respects (*e.g.* in reflection and refraction) just like a continuous train of waves. If the radiation is monochromatic, *i.e.* of one wavelength only, then in accordance with Planck's equation the energy quanta must all have the same value.

Atomic spectra consist of a limited number of lines, each corresponding to the emission of radiation of a particular wavelength. It follows from the quantum theory that the atoms can only emit energy in certain definite amounts. It was as a result of this deduction that Bohr in 1913 proposed an explanation of atomic spectra in terms of the arrangement of the electrons in atoms. He suggested that the electrons could only exist in certain definite energy states, or *energy levels*. If a sodium atom, for example, is heated in a flame, it can only absorb energy in the exact amount needed to raise the energy of an electron to some higher level. In this way, heat energy is transformed into what is called electronic energy. The electron will not remain at the high level, but will fall back either to the level from which it started or to some intermediate level, and in so doing will lose an amount of energy exactly equal to the difference between the two energy levels. This energy will be emitted as a quantum of radiation of a definite wavelength. If there are many energy levels, many alternative transitions between levels will be possible and radiation of several different wavelengths will be emitted, thus giving a spectrum.

2.10. Atomic energy levels

The differences between different energy levels can be found very accurately by measuring the wavelengths of the spectral lines, and so an energy level diagram can be constructed. Fig. 3 shows such a diagram for hydrogen, together with a portion of the hydrogen spectrum showing the energy transitions which have produced the lines given. The arrows represent the amount of energy emitted for a particular transition: the greater the energy, the higher will be the frequency of the radiation (and therefore the smaller the wavelength) in accordance with Planck's equation. The dotted arrows show other possible transitions, which give lines in the ultra-violet (high energy) and infra-red (low energy) regions of the spectrum.

By considering the spectra of different elements, together with the number of electrons that the atoms are known to contain, it has been possible to build up a complete picture of the possible energy states of

an electron in an atom. It must be remembered that this does not tell us the *position* of the electron, but only its energy state. It will be shown later that it is not possible to fix the actual position of electrons exactly, but broadly speaking the electrons can be regarded as occupying

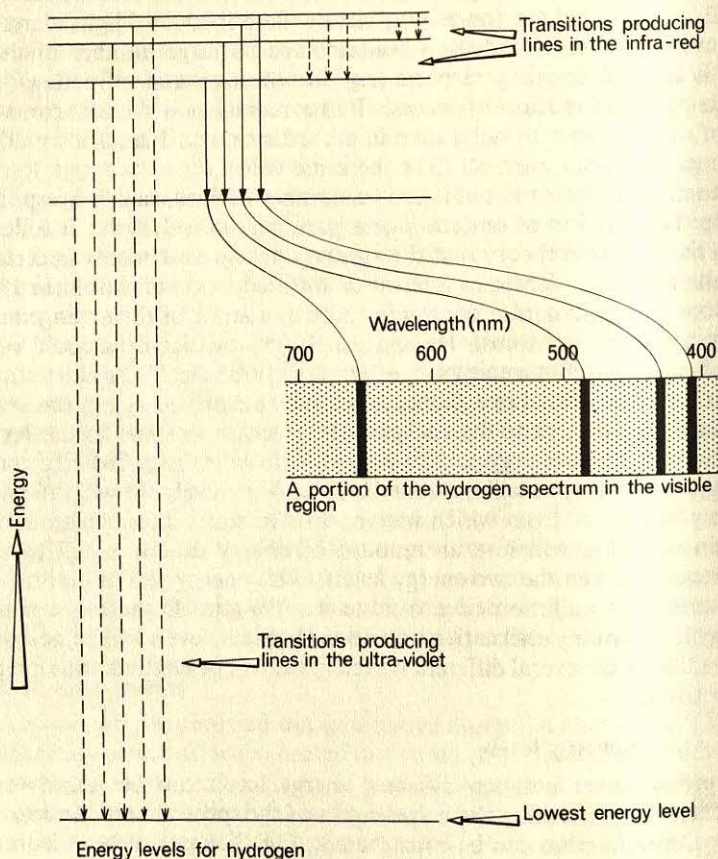


Fig. 3. Energy level diagram for hydrogen, and part of the corresponding spectrum

spherical "shells" around the nucleus (Fig. 4). The shells are known by the letter K, L, M, etc., starting from the one nearest to the nucleus, or alternatively by the *principal quantum numbers* 1, 2, 3, etc. It will be seen from Fig. 4 that, with the exception of the K shell, each shell contains a collection of energy levels labelled *s*, *p*, *d* or *f*. These represent levels of different energy at the same principal quantum number. An *s* level in the K shell is written 1*s*, a *d* level in the O shell 5*d*, and so on.

Now suppose that we could take the nucleus of an atom and feed in the correct number of electrons one at a time. The electrons would go to the positions of least energy, so that the lowest energy levels would be filled first, then the next lowest, and so on. This can be compared with a number of balls rolling down some steps: the first balls will reach the bottom, but when the bottom step is filled the next balls will stop on the step next higher up, and so on until the supply of balls is used up. In order to find out the final arrangement of the electrons all we need to know is (a) the order in which the levels occur in terms of energy, and (b) how many electrons each level will accommodate.

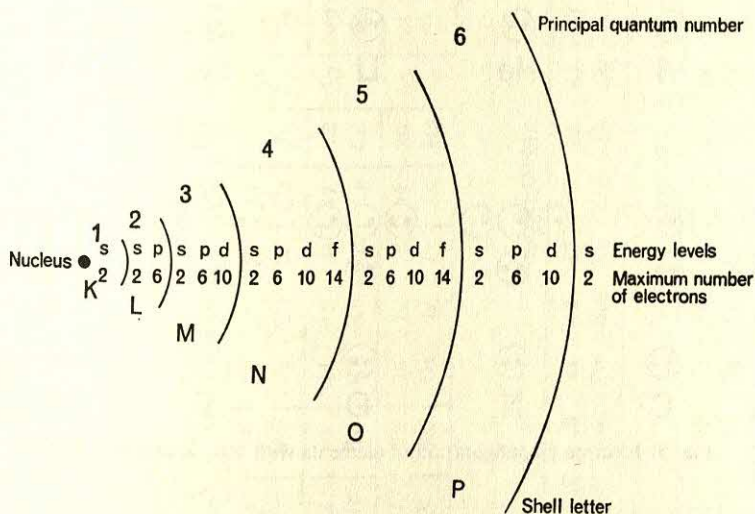


Fig. 4. Electron shells of an atom, showing the number of electrons that can be accommodated in the various energy levels

The order of the levels, in increasing energy, is almost as shown in Fig. 4, *i.e.* $1s-2s-2p-3s-3p$, but after this there is some intermingling of the levels of different shells, *i.e.* $4s-3d-4p-5s-4d-5p$. The number of electrons accommodated is decided by the type of level: *s* levels can have a maximum of two electrons, *p* levels six electrons, *d* levels ten electrons, and *f* levels fourteen electrons. The electrons in atoms of atomic numbers 1 to 10 will therefore occupy the energy levels shown in Fig. 5. The first two electrons go into the $1s$ level (H and He), the next two into the $2s$ level (Li and Be), and the next six into the $2p$ level (B to Ne).

It will be noticed that the *p* electrons have been put into three separate "boxes"; this is because there are actually three energy levels here. It is now known that no two electrons can be in exactly the same energy state, but owing to the fact that an electron can also have "spin" energy

(this may be imagined as being caused by the electron spinning about an axis) each energy level can be occupied by two electrons having spins in opposite directions. Similarly, *d* levels contain up to ten electrons because there are five separate energy levels, with a maximum of two electrons in each.

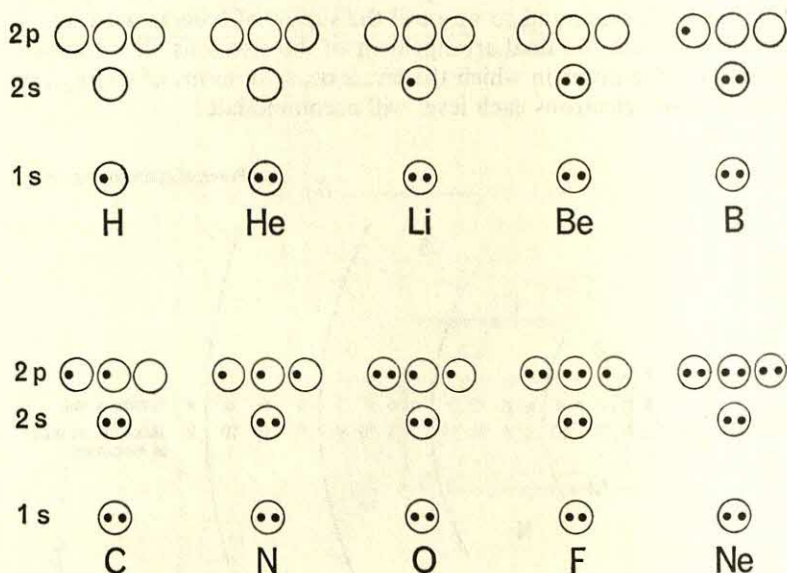


Fig. 5. Electronic configuration of elements with atomic numbers 1-10

2.11. Electronic structure and the periodic table

We can now see how the periodic variation of properties in the elements can be explained in terms of the electronic structure of the atoms. Fig. 6 shows the complete periodic table, giving each element with its atomic number. The arrows at the side of certain groups indicate the point at which the various sets of energy levels start being occupied. Thus in the first period the electrons go into the *1s* level, and with helium (two electrons) this is filled. In the second period the *2s* level contains one electron for lithium and two electrons (filled) for beryllium: the next electrons go into the *2p* levels starting with boron, and these levels are filled when they contain six electrons (neon).

Turning to the chemical properties, the members of each of the main groups (IA, IIA, IIIB, IVB, VB, VIB, VIIB, and the noble gases) closely resemble one another. A glance down the table shows that the electronic structure of each member of a particular group has one point in common: the outermost electron shell contains the same number of electrons in the same energy states:

Group	IA	IIA	IIIB	IVB	VB	VIB	VIIB	noble gases
Outer shell } <i>s</i>	1	2	2	2	2	2	2	2
electrons } <i>p</i>			1	2	3	4	5	6

We may deduce from this that the inner filled shells of electrons do not take part in chemical reactions, and that the chemical properties are decided by the electrons in the outer shell. The latter can therefore be called the *valence electrons*. When both *s* and *p* levels are completely filled, as is the case for the noble gases, the atom becomes chemically unreactive.

Hydrogen and helium do not quite fit into this scheme because the K shell contains only the single *1s* level. However, since this level is filled in the helium atom, the electronic structure of helium is similar in this respect to the noble gases, thus justifying its position as the first member of this group. Hydrogen can be regarded either as having a single *s* valence electron (similar to group IA), or as being one short of a filled shell (as in group VIIB). Hydrogen has, in fact, some properties in common with each of these groups. The best position for hydrogen in the periodic table is open to argument, and it may be either classed with one or both of the groups mentioned above, or left on its own.

At the end of the third period in the table the *3s* and *3p* levels are full. After this, the order in terms of increasing energy is *4s-3d-4p-5s-4d-5p*, so that the next two electrons go into the *4s* level (potassium and calcium). The *3d* levels are now filled, starting with scandium and finishing with zinc; these ten elements are placed in the transition block. The difference in energy between *3d* and *4s* is not large, and sometimes the *4s* is not filled:

Element	Sc	Ti	V	Cr	Mn	Fe	Co	Ni	Cu	Zn
Number of } <i>3d</i>	1	2	3	5	5	6	7	8	10	10
electrons } <i>4s</i>	2	2	2	1	2	2	2	2	1	2

The almost constant number of electrons in the outer shell, together with unfilled levels in the underlying shell, give these elements many properties in common. The three elements iron, cobalt and nickel are included in what are called the *transitional elements* (group VIII), although from an electronic point of view all ten elements form a transition block. It has been found convenient to treat the elements scandium to manganese as the first members of *sub-groups* to the main groups III-VII, although they resemble their neighbouring transitional elements more closely than the groups to which they are thus attached. The same applies to copper. Zinc, on the other hand, has an electronic structure closely resembling that of group IIA so that there is more

justification for its inclusion in sub-group IIB. The rest of the elements in the transition block have similar electronic arrangements to those of the fourth period, arising from the filling of the $5s$ levels before the $4d$, and the $6s$ before the $5d$.

Two further groups of elements are shown at the foot of the table. The first follow lanthanum in order of atomic number, and are called the *lanthanides* or rare earths. In this series of elements the $4f$ levels are being filled, because these are of higher energy than the $6s$ but slightly lower than the $5d$. The outermost shell contains two $6s$ electrons in all the fourteen members of this series, whereas the incompletely filled $4f$ levels are shielded by a completed $5s$ and $5p$ shell. Consequently all the lanthanides have very similar chemical properties. This is an example of an *inner transition series*; another one starts at the corresponding place in the next period, after actinium, the elements of this series being called *actinides*. Uranium is the last element in this series that occurs in nature, and the rest have all been made artificially by nuclear reactions (§ 2.6).

2.12. The Bohr atom

Rutherford, and later Bohr, thought that the electrons in an atom were in constant motion around the nucleus in closed orbitals, like a satellite in orbit around the earth. Bohr showed that orbits of small radius would have the least energy, so an electron in the lowest energy state would be nearest to the nucleus, the distance increasing in definite steps for the higher levels. When this model of the atom was first produced, Bohr's knowledge of the energy levels was incomplete and he assigned only one orbit to each principal quantum number. The treatment was later modified but, since the idea of electrons moving in orbits was later shown to be incorrect, only the simplified picture will be given here. In this, each orbit represents a complete electron shell, and will therefore contain a maximum of 2, 8, 18, etc., electrons (for the K, L, M, etc., shells). The Bohr picture of some simple atoms is shown in Fig. 7.

Although the Bohr atom has now been superseded, it can still be

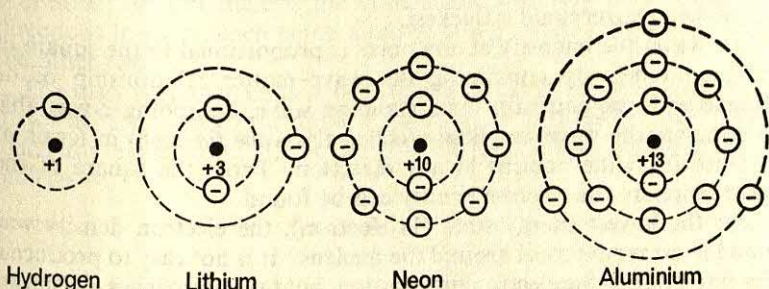


Fig. 7. Representation of atoms according to Bohr

used as a convenient way of showing, in a simple pictorial form, the numbers of electrons in the different shells and it will be used for this purpose later in this book.

2.13. The wave nature of the electron: orbitals

There are two serious objections to the Bohr idea of an electron circulating in a closed orbit. First, there are theoretical reasons why such a system would not be stable. Second, it is now known that electrons in motion behave as though they were small parcels of radiation, in other words they have a wave form. This was first proved in 1927, when Davisson and Germer showed that when a beam of electrons was reflected from a crystal a regular diffraction pattern was obtained, just as occurs when x-rays are reflected from a crystal (§ 7.2).

It is not only electrons that behave in this manner. We have already seen that radiation has properties which can be associated with both waves and small packets (or "particles") of energy. In 1923, de Broglie suggested that particles of matter would also behave like waves, and he showed that the wavelength should be inversely proportional to the momentum (mass $\times$ velocity) of the particle. The experiment with electrons referred to above showed that this theory was correct, and it has since been demonstrated that beams of other light particles (*e.g.* neutrons) have a wave form.

The wave theory of the electron at once removed the difficulty of imagining an electron travelling in a closed path, as this is quite possible for a wave, providing the path is equal to a whole number of wavelengths (this is what is known as a standing wave). Moreover, when the wavelengths of the electrons in the Bohr atom were calculated, using de Broglie's relationship, it was found that they fitted exactly into the Bohr orbits.

Another consequence of the wave theory is that it is no longer possible to fix the actual position of the electron, since a wave is not confined to a particular point but is spread out in space. The electron is, as it were, smeared out in the space surrounding the nucleus as a diffuse cloud. We can no longer think of the electron as being in any particular place, but must approach the problem in a different way, by finding out where the electron cloud is thickest.

In a wave, the intensity at any point is proportional to the square of the amplitude. By combining the wave-matter relationship of de Broglie with the equation for a standing wave, Schrödinger was able to calculate the wave amplitude (called the *wave function*) in terms of distance from the nucleus in any direction. From the square of the wave function, the *electron density* can be found.

For the lowest energy state (1s electron), the electron density was found to be symmetrical around the nucleus. It is not easy to produce a simple picture of the electron distribution, but two approaches are shown in Fig. 8. One represents the density of the electron cloud by means of

shading, while the second is an outline of the shape of the cloud. Both are cross-sections of the cloud, which is actually spherical. These pictures represent what are known as atomic *orbitals*. Other *s* orbitals ($2s$, $3s$, etc.) are also spherical, but with the highest electron density farther from the nucleus.

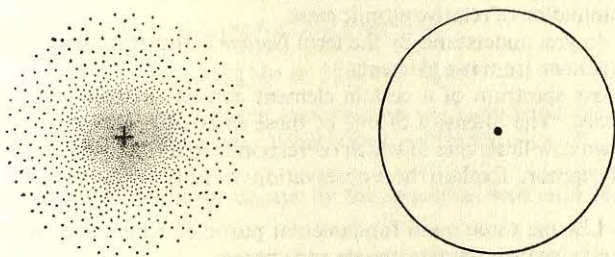


Fig. 8. Electron orbitals for *s* electrons

The orbitals for *p*, *d* and *f* electrons are not symmetrically distributed, but are directed in space in certain definite directions. We shall only be concerned with the *p* orbitals, which are shaped rather like a pair of dumb-bells projecting on opposite sides of the nucleus (Fig. 9). As

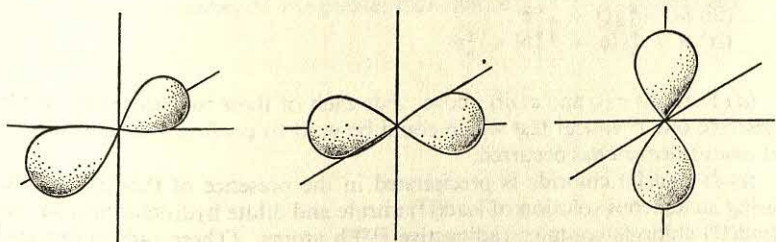


Fig. 9. Electron orbitals for *p* electrons

there are three separate energy levels for *p* electrons, so there are three *p* orbitals: each of these is the same shape, but they occupy different directions in space, each being directed along an axis at right angles to the other two.

The discovery that certain orbitals had directional character was a major achievement of the application of the wave theory, since it provided the explanation of the fixed bond angles that are observed in molecules.

QUESTIONS

G.C.E.

1. Outline the use of the mass spectrometer in the determination of relative atomic mass.

Explain briefly why $H = 1$ and $O = 16$ are no longer used as standards for the determination of relative atomic mass.

What do you understand by the term *isotope*? Illustrate your answer with examples drawn from two elements.

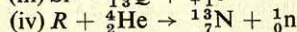
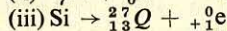
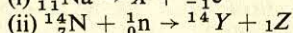
The mass spectrum of a certain element consists of a number of closely spaced lines. The intensity of one of these lines decreases over a period of time as two new lines, one of which corresponds to a relative mass of 4, simultaneously appear. Explain these observations as fully as you can.

[Cambridge]

2. (a) List the three main fundamental particles which are constituent of atoms, and give their relative masses and charges.

(b) Similarly, name and *differentiate* between the radiations emitted by naturally occurring radioactive elements.

(c) Complete the following equations using your periodic table to identify the elements X , Y , Z , Q and R . Add atomic and mass numbers where these are missing:



(d) Refer to c (i) and c (iii) above. For each of these two processes, briefly describe ONE chemical test which could be used to confirm that a change of chemical element has occurred.

(e) If lead(II) chloride is precipitated in the presence of thorium nitrate, using an aqueous solution of lead(II) nitrate and dilute hydrochloric acid, the lead(II) chloride contains radioactive ${}^{212}\text{Pb}$ atoms. (These radioactive lead atoms are a daughter product of the thorium.)

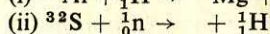
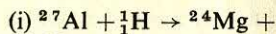
Show how you could experimentally use this information to establish that lead(II) chloride and its saturated solution are in dynamic equilibrium.

[S.U.J.B.]

3. (a) Explain how ${}^{235}\text{U}$ can be used to produce (i) energy at a controlled rate, (ii) an explosion.

(b) How is the radio-isotope ${}^{14}\text{C}$ produced in nature and how are its properties made use of in radiocarbon dating?

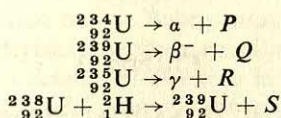
(c) Complete the following nuclear equations, adding all the missing mass numbers, atomic numbers and symbols:



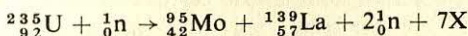
[Cambridge]

4. (a) What are α , β and γ emissions and how do they differ in their penetrating power and their behaviour in a magnetic field?

Explain the meaning of the two numbers before the symbol for uranium and identify P , Q , R and S in the following equations.



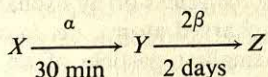
(b) Deduce the nature of X in the following reaction.



There is approximately 0.1 per cent less mass on the right-hand side of the equation than on the left-hand side. What is the significance of this?

[J.M.B.]

5. A radioactive element, X , decays by the sequence, and with the half-lives, given below:



Which of the following statements about this system are correct?

1. After two hours, less than 10% of the initial X is left.
2. The maximum amount of Y present at any time is less than 50% of the initial amount of X .
3. The atomic numbers of X and Z are the same.
4. The mass number of Y is greater than that of X .

[Cambridge]

CHAPTER 3

THE CHEMICAL BOND

3.1. Valence

Although we can regard the atom as the basic chemical unit, atoms rarely exist in the free state at ordinary temperatures. The noble gases are exceptional because they are chemically unreactive, but the atoms of all other elements show a strong tendency to combine, either with each other or with the atoms of other elements. This they do either by linking together to form *molecules* or by exchanging electrons to form positively or negatively charged atoms, *i.e.* *ions*. The term *molecule* is usually defined as the smallest particle of an element or compound that normally exists in the free state. In the case of the noble gases the atom is the stable form, so that the atom and the molecule are the same. We also speak of the molecule of ionic compounds such as sodium chloride, although it will be seen later that this description is not strictly correct.

The stability of a molecule is due to the strong forces which hold together the atoms of which it is composed. These forces are called *chemical bonds*, or *valence bonds*, and the number of bonds in which an atom can take part is the *valency*. Hydrogen has a valency of one (as in the hydrogen molecule H_2 , where a single bond unites the two atoms), so that the valency of an atom can be defined as the number of atoms of hydrogen that the atom will combine with or replace. The valencies of atoms are related to their electronic structure, as can be seen by reference to the periodic table. In each of the main groups, all the members of a group have the same number of *s* and *p* valence electrons, and all are found to exhibit the same valency. In the transition block, however, the valencies are variable: this is because there is the possibility of electrons in the partly-filled inner levels also taking part.

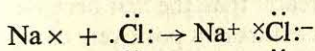
The electronic theory of valence was first put forward by Lewis in 1916 and later developed by Sidgwick. They worked on the principle that the electronic structure of the noble gases (eight electrons in the outer shell) represented a stable arrangement, and that the atoms of other elements would react together in order to achieve the same stable "octet". This may occur in one of two ways: (a) electrons can be transferred from one atom to another until both have an outer shell of eight (this type of valence leads to the formation of ionic compounds, and is known as *electrovalence*); (b) the atoms can share electrons in order to complete their shells (the shared electrons constitute a definite bond between the atoms, and this is known as *covalence*). In the case

of hydrogen the stable shell contains only two electrons, corresponding to the noble gas structure of helium.

This treatment is based on the Bohr picture of the atom and takes no account of the differences between *s* and *p* electrons. However, it predicts correctly the valencies of elements in the main groups of the periodic table and is a useful way of showing the number of valence electrons involved in bond formation. For some purposes, however, it is inadequate and the atomic orbital interpretation must be used. In the examples that follow, both the Lewis method (Bohr atom) and orbitals will be used as occasion demands.

3.2. Electrovalence

An example of electrovalence is the formation of sodium chloride from sodium and chlorine atoms. Sodium has one valence electron, and if it loses this it is reduced to the underlying inert gas structure. Chlorine, with seven valence electrons, lacks one electron to make a stable octet. The following equation shows the result of transferring an electron from the sodium to the chlorine (it is convenient to show the valence electrons as dots or crosses so that it can be seen to which atom they originally belonged, but it must be remembered that all electrons are actually the same and indistinguishable from one another):

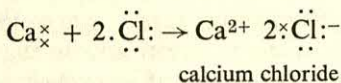


By losing its valence electron, the sodium atom has acquired the same electronic structure as the noble gas neon; the nucleus still has its eleven positive charges, and since there are now only ten electrons there is a single positive charge on the sodium ion that has been formed. The chlorine atom, having gained an electron, becomes a chloride ion with a single negative charge and the noble gas structure of argon. The ions that have been formed are more stable than the original atoms because they have a more stable electronic structure.

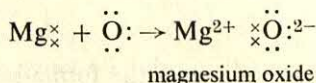
It should be noted that the sodium and chloride ions are not directly attached to each other. No actual bond has been formed. The fact that the ions are of opposite charge does, however, cause a strong force of electrostatic attraction between them. In the solid or liquid state, ionic substances consist of a mixture of positive and negative ions held together by these forces, and since electrostatic forces are non-directional each positive ion will attract any negative ions that are close to it, and vice versa: this is clearly shown by the crystal structure of sodium chloride (*see* p. 97). It is thus impossible to say that any one ion is attached to any other, so that the term "molecule" has no real meaning when applied to ionic materials, and if we speak of the molecule of sodium chloride we really mean the ion-pair Na^+Cl^- . In most equations, however, it does not lead to any confusion if it is simply written NaCl .

The metals of group IIA (Be, Mg, Ca, etc.) have two valence electrons,

and both of these can be transferred to atoms capable of accepting them, thus forming doubly-charged positive ions:



Doubly charged negative ions can be formed from atoms of group VIB (O, S, etc.) which have six valence electrons (two short of the stable octet):



The removal of an electron from an atom requires the expenditure of a certain amount of energy. This is usually expressed in terms of the *ionisation energy*, which is the energy needed to remove an electron from an atom in the gaseous state. The ionisation energy can be deduced from the energy levels derived from spectra, because the electron is freed from the atom when it has reached an energy just greater than that of the highest level. If a second electron is removed, the second ionisation energy is greater than the first because the negatively charged electron has to be ejected from a positively charged ion. The following figures give the ionisation energies for the removal of the valence electrons from three metal atoms, containing respectively one, two and three valence electrons. The units are kilojoules per mole.

Element	Na	Mg	Al
1st ionisation energy	490	730	580
2nd ionisation energy		1450	1810
3rd ionisation energy			2740

The energy that is needed to produce the positive ion has to be supplied from some other part of the process: for example, energy may be released when the other atom in the reaction accepts the electron, and if a solid ionic compound is formed energy will also be obtained from the work done by the electrostatic forces. The ionisation energies for aluminium show the increasing difficulty of removing the second and third electrons, and there is not usually sufficient energy available to form positive ions with more than two charges. For this reason, trivalent and tetravalent metal ions are uncommon in the solid state, although they may occur as hydrated ions when a covalent compound is dissolved in water.

The charge on a simple negative ion, *i.e.* one that is formed from a single atom, is also limited because of the difficulty of adding further electrons to a body that is already negatively charged. Such ions cannot have more than two charges (*e.g.* O^{2-} , S^{2-}), although more complex

negative ions can have a greater number (e.g. phosphate, PO_4^{3-} ; silicate, SiO_4^{4-}).

Electrovalent compounds consist of charged particles (ions) held together by strong electrostatic forces, and this gives them the following characteristic properties:

(a) High melting point, and extremely high boiling point. This is because a considerable amount of energy is required to separate the ions.

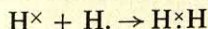
(b) They conduct electricity when molten, in which state the ions are free to move.

(c) They are readily soluble in liquids of high permittivity (e.g. water), but almost insoluble in liquids of low permittivity (e.g. benzene, ethoxyethane) (see § 8.1).

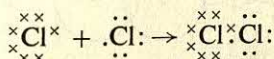
(d) Their solutions conduct electricity.

3.3. Covalence

When atoms combine to form molecules they do so by sharing electrons, thus forming what are called *covalent bonds*. The simplest example of such a bond is in the hydrogen molecule, where the sharing of the two single electrons completes the electron shells of both atoms:



The formation of a chlorine molecule can be represented in a similar way, each atom sharing one electron with the other to complete the two octets:



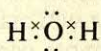
The bond, in each case, consists of one pair of shared electrons. Atoms with seven valence electrons have only one vacant space, and can only take part in one bond: they have a *covalency* of one. With one electron less (six valence electrons, as in oxygen) two bonds are possible, and so on down to carbon, where all four electrons can take part in bond formation:

Group VII B
(7 valence
electrons)



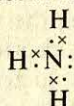
hydrogen
chloride

Group VI B
(6 valence
electrons)



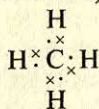
water

Group V B
(5 valence
electrons)



ammonia

Group IV B
(4 valence
electrons)



methane

Beyond carbon there are less than four valence electrons, so that an octet can be achieved only by accepting electrons from other atoms:

the way in which this can occur with group IIIB elements (*e.g.* aluminium) will be shown later in this section.

As already explained, this treatment of covalence has its limitations. Though it has been successful in explaining the number of covalent bonds that many atoms can take part in, there are several important points for which it cannot account:

(a) The theory supposes that covalent bonds are due to electrons shared between atoms, but cannot explain *why* this should occur.

(b) Since the Bohr atom tells us nothing about the relative positions of electrons in the valence shell, the directions of the bonds cannot be predicted. Yet it is known that the bonds in molecules are at definite angles to one another.

(c) It would appear that all electron-pair bonds should be alike: we shall see later that this is not the case.

All these points can be explained if the Bohr atom is replaced by the atomic orbital approach.

Taking again the hydrogen molecule as an example, each hydrogen atom, before reaction, has one *s* electron which can be represented by a spherical *s* orbital. If the atoms can approach within a certain distance, their orbitals will overlap (Fig. 10) and since each electron can

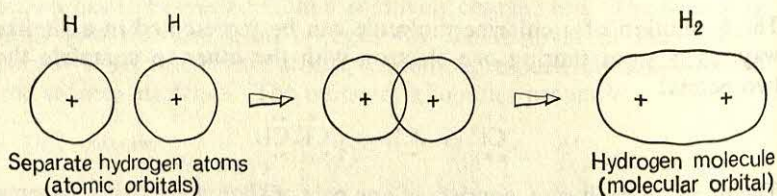


Fig. 10. Formation of a hydrogen molecule, shown in terms of electron orbitals

be anywhere within its orbital it is possible for an exchange of electrons to take place. The electrons are no longer attached to their original atoms, but are shared between them. So far we are merely imagining that this might take place, but the great advantage of the wave theory of the electron is that it is possible to calculate whether overlap (electron sharing) is possible, and what the result would be: this is done mathematically by combining the wave functions of the two electrons. The calculation shows that electron-sharing will cause the two atoms to be drawn together. It would actually be more correct to say that the two *nuclei* are drawn together, since the original atoms no longer exist as separate entities: the two electrons form a single electron cloud surrounding both nuclei, and now occupy a new *molecular orbital* (see Fig. 10). The two nuclei cannot approach each other too closely, because at short distances there is strong repulsion due to the fact that they are both

positively charged. The distance between the nuclei will be fixed by a balance between attraction and repulsion, at the value that gives the minimum energy.

The formation of a covalent bond is thus due to a lowering of energy as a result of overlap of orbitals. With s orbitals (as in the formation of the hydrogen molecule) this simply means that the two atoms must be very close to each other; as the orbitals are spherical the direction of approach does not matter. The case is different for p orbitals, for these are concentrated in certain definite directions and effective overlap can only take place with the orbital of an atom approaching from the correct direction.

The directional nature of bonds formed from p orbitals can be illustrated by the formation of hydrogen chloride, water and ammonia (Fig. 11). The orbitals that are shaded contain two electrons and therefore cannot form a bond with a hydrogen atom: this is because the final molecular orbital will only take two electrons, of which one is supplied by the hydrogen and the other by an orbital of the other atom containing one electron only. *Hydrogen chloride*: chlorine has five p valence electrons, which will fill two p orbitals (two electrons each) and leave one orbital available for bonding (one electron). The latter is shown overlapping with the s orbital of the hydrogen. *Water*: the four

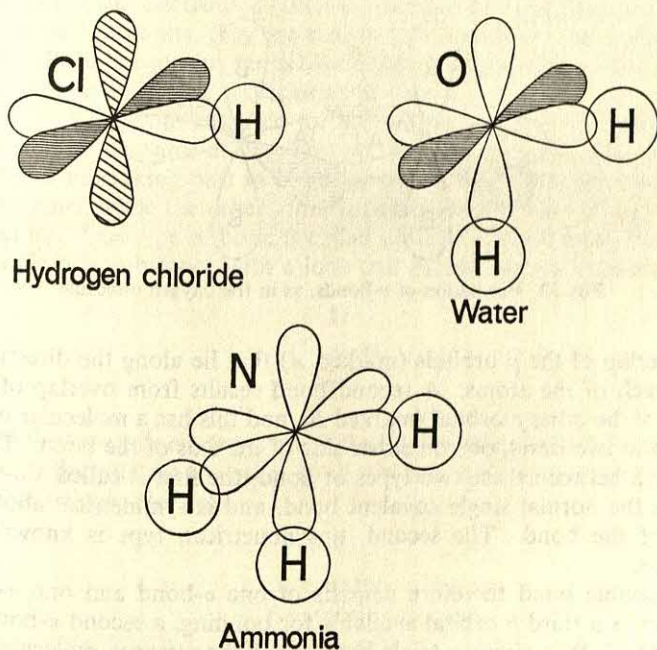


Fig. 11. The directional nature of bonds formed with p orbitals

p electrons of oxygen can be arranged so as to fill one orbital, leaving the other two orbitals with one electron each. The two O—H bonds that are formed should therefore be at right angles. *Ammonia*: nitrogen has only three p electrons, so that all three orbitals are available for bonding, and the three N—H bonds are again at right angles so that the ammonia molecule has a pyramidal shape.

Measurements show that the actual bond angles in water and ammonia are rather more than 90° . This is partly due to repulsion between the hydrogen atoms, and partly because the orbital overlap picture has ignored the possibility of the s electrons of the oxygen and nitrogen also taking part to a small extent. The bonds are actually partly *hybrid*, which is a term used to describe bonds involving different types of orbital from the same atom.

Carbon has a total of four valence electrons and, to obtain the maximum number of orbitals for bonding, three of these must be put into the three p orbitals, leaving the s orbital with one electron. In this case there is complete hybridisation, the one s and three p orbitals combining to form four identical orbitals all directed at equal angles to one another. Overlap with these gives the tetrahedral valences of carbon.

Sometimes more than one bond is formed between two atoms, as in the case of the oxygen molecule (Fig. 12). One of the bonds is formed

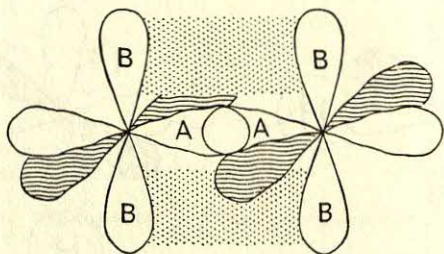


Fig. 12. Formation of π -bonds, as in the oxygen molecule

by overlap of the p orbitals (marked A) that lie along the direction of approach of the atoms. A second bond results from overlap of both parts of the other p orbital (marked B), and this has a molecular orbital that is in two parts, one on either side of the axis of the bond. To distinguish between these two types of bond, the first is called a σ -bond: this is the normal single covalent bond, and is symmetrical about the axis of the bond. The second, unsymmetrical, type is known as a π -bond.

A double bond therefore consists of one σ -bond and one π -bond. If there is a third p orbital available for bonding, a second π -bond can be formed, thus giving a triple bond (as in the nitrogen molecule).

A special case of π -bonding occurs in benzene, where the p orbitals

of each of the six carbon atoms can overlap with those on either side. This means that the six electrons concerned are shared by all six carbon atoms at the same time, so that the π -bonding is continuous all round the ring (Fig. 13). This gives an increased stability to the benzene mole-

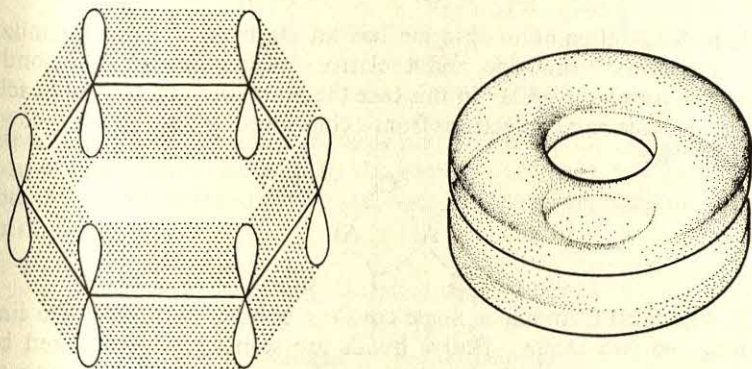
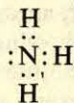


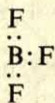
Fig. 13. π -bonds in benzene

cule. Since the electrons in such a bond are not confined to any particular pair of atoms, they are said to be *delocalised*. Delocalisation is not confined to benzene, but is found in aromatic compounds in general, and in many inorganic molecules and ions.

The two electrons required for a covalent bond are sometimes both provided by the same atom. This can happen when one atom has two electrons not taking part in bond formation (these electrons are called a *lone pair*), while the other atom is two electrons short of an inert gas structure. This type of bond is called a *dative* or *co-ordinate* bond. An example of a substance with a lone pair of electrons is ammonia

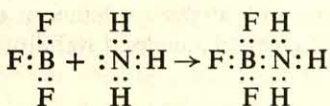


where the lone pair electrons are in the filled p orbital. In the compound boron trifluoride, on the other hand, the boron atom is associated with only six valence electrons

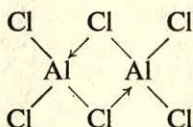


and can accept the lone pair to complete the octet. Ammonia and boron

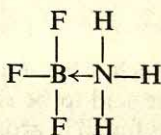
trifluoride are both gases, but when mixed they react to form a solid addition compound:



Anhydrous aluminium chloride has an electronic structure similar to that of boron trifluoride, and a relative molecular mass corresponding to the formula Al_2Cl_6 . In this case the aluminium atoms have each accepted a lone pair of electrons from a chlorine atom, giving the following structure:

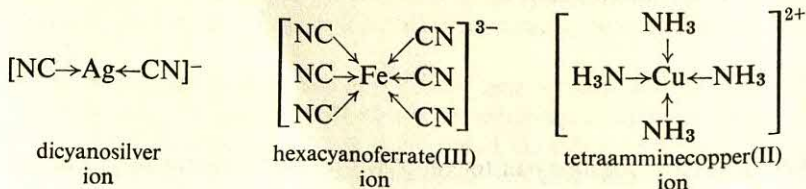


In structural formulae a single covalent bond is indicated by a line joining the two atoms. Dative bonds are sometimes represented by arrows, pointing towards the atom that has accepted the lone pair of electrons:

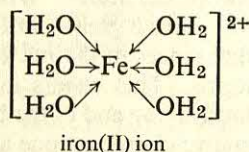
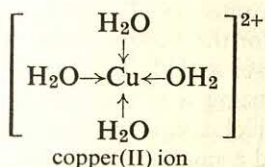


This does not mean that there are two different types of bond in the above compound: once a dative bond has been formed it is a normal covalent bond, and it does not matter where the two shared electrons have come from.

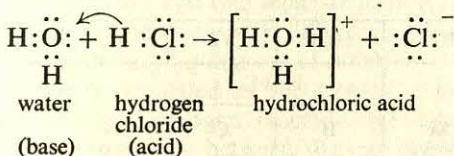
Ions of the elements in the transition block have many unfilled orbitals, and therefore readily combine with groups which have lone pair electrons available. In this way they form complex ions with molecules and ions such as water, ammonia, the cyanide ion and many others. The Lewis method of showing the electron pairs is not very useful for these complexes, as the number of electrons shared by the acceptor atom may be one of several possible values. This is because the Lewis octet rule only applies to shells of *s* and *p* electrons, whereas with the transition elements *d* electrons are also involved. The following examples of complex ions show the dative bonds:



Many positive ions form complexes with water in the same way, and they exist in this hydrated form both in the solid hydrated salt and in solution. Examples are:



Reactions between acids and bases involve the transfer of a proton (hydrogen ion) from the acid to the base (§ 14.6), and this provides another example of the dative bond, with the base supplying the lone pair of electrons:



Note that water can act as a base, and that the hydrogen ion in solution is in the form of the hydrated ion H_3O^+ . The latter is sometimes called the *hydronium ion*, but more often is simply referred to as a "hydrogen ion," it being understood that in aqueous solution it is always in the above form.

The dative bond is less common in organic compounds. Examples of groups containing such bonds are nitro compounds and amine oxides, e.g. $(\text{CH}_3)_3\text{N} \rightarrow \text{O}$.

The properties of purely covalent compounds differ in many respects from those of ionic (electrovalent) compounds. This is because they exist as molecules. The attractive forces between molecules are weaker than the electrostatic forces between ions, since molecules carry no electric charge. The general characteristics of covalent compounds are:

(a) Because of the definite length and direction of the bonds, molecules have a definite shape.

(b) Melting and boiling points are much lower than those of ionic compounds, because less energy is needed to separate the molecules.

(c) Solubility varies widely, but in general non-polar solvents are the most effective: comparatively few covalent compounds are soluble in water, apart from those that form hydrogen bonds with water molecules.

(d) Solutions are non-ionic and therefore do not conduct electricity, except in cases where reaction occurs with the solvent (e.g. acids and bases).

3.4. Dipole moments

When a covalent bond is formed between two atoms of the same element, as in the hydrogen molecule, the two electrons are shared equally between the atoms. When the atoms are of different elements, one atom will have a greater attraction for the electrons than the other, owing to differences in the nuclear charges and electronic structures of the two atoms. This results in there being a greater density of the electron cloud at one end of the bond, which is equivalent to there being a small negative charge on one atom and a small positive charge on the other. Such a bond is said to be *polar*. The extent to which it occurs depends on the relative attraction that different atoms have for electrons: this is known as the *electronegativity*. Table 1 gives the relative electronegativities of many elements, as calculated by Pauling. The elements

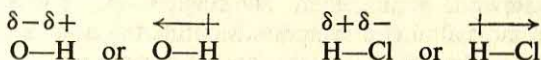
TABLE 1. ELECTRONEGATIVITIES

IA	IIA	IIIB	IVB	VB	VIB	VIIB
		H 2.1				
Li 1.0	Be 1.5	B 2.0	C 2.6	N 3.0	O 3.5	F 4.0
Na 0.9	Mg 1.3	Al 1.5	Si 1.9	P 2.2	S 2.6	Cl 3.2
K 0.8	Ca 1.0		Ge 1.9	As 2.1	Se 2.5	Br 3.0
Rb 0.8	Sr 1.0		Sn 1.9	Sb 2.0	Te 2.3	I 2.7
Cs 0.7	Ba 0.9		Pb 1.8	Bi 1.9		

have been put in the order of the periodic table, and it will be seen that there is a regular increase in electronegativity from left to right. This can be connected with the fact that elements near the left of the periodic table readily form positive ions, *i.e.* their attraction for electrons is low, while elements on the right of the table form negative ions, showing that they have a high electronegativity.

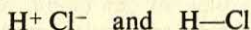
The polarity of a covalent bond is related to the difference in electronegativity of the two atoms concerned. The larger the difference, the greater will be the displacement of electrons towards the atom with the higher electronegativity. Thus in the O—H bond (as in alcohols and the water molecule) the electronegativity difference between oxygen and hydrogen is $3.5 - 2.1 = 1.4$. The oxygen, having a much greater electronegativity than hydrogen, will have a considerably larger share of the electron pair and the bond will be strongly polar, with the oxygen carrying a partial negative charge and the hydrogen a partial positive charge. When the difference in electronegativity is small, as in the case of the C—H bond in methane (difference $2.6 - 2.1 = 0.5$), the bond is only weakly polar.

When writing the structural formula of a molecule, it is often desirable to show the polarity of the bonds, and this can be done in two ways: either by indicating the position of the charges (these are written $\delta+$ and $\delta-$ since they are only a fraction of an electronic charge), or by drawing an arrow pointing in the direction in which the electrons have been displaced and with a bar at the positive end:



It will be seen that the greatest difference in electronegativity occurs between elements at opposite ends of a period (e.g. sodium and chlorine, difference 2.3). When two such atoms react together the very strong attraction that one atom has for an electron, coupled with the relatively weak attraction of the other atom, results in the transfer of an electron from one atom to the other and two separate ions are formed (electrovalence). When the electronegativity difference is smaller, covalent bonds are formed, with varying degrees of polarity.

A polar bond can be regarded as being partly covalent and partly ionic. The molecule of hydrogen chloride, for example, could be depicted as being intermediate between the completely ionic and the purely covalent forms:



In the same way, electrovalent compounds may have a proportion of covalent character. There is no clear distinction between ionic and covalent bonding, and all types of intermediate bond are possible.

The electrical moment of a polar bond is known as the *dipole moment*, measured in units of charge (coulombs) multiplied by distance (metres). Dipole moments are also commonly expressed in Debye units (D), where $1 \text{ D} = 3.34 \times 10^{-30} \text{ C m}$. The dipole moment of a bond, in Debye units, is approximately equal to the difference in electronegativity between the two atoms. Thus in hydrogen chloride the electronegativities are 3.2 for chlorine and 2.1 for hydrogen, difference 1.1, while the measured value of the dipole moment is 1.03 D ($3.44 \times 10^{-30} \text{ C m}$).

3.5. Bond lengths and bond strengths

It is difficult to define what is meant by the size of a molecule, because the electrons are not confined to a definite region in space. The electron density falls off rapidly after a certain distance from the nuclei, but no sharp boundary can be drawn. However, the distances between the atomic nuclei, i.e. the *bond lengths*, are fixed when the bonds are formed and can be measured accurately by x-ray methods (§ 7.2). It is therefore usual to measure the dimensions of molecules in terms of the bond lengths, expressed in picometre units ($1 \text{ pm} = 10^{-12} \text{ m}$). Measurements show that the length of a single covalent bond between any two given atoms is approximately the same (within a few picometres)

no matter what the nature of the rest of the molecule may be (an exception to this rule occurs where there are delocalised π -bonds, as in the benzene molecule).

A selection of covalent bond lengths is shown in Table 2. It will be seen that multiple bonds are shorter than the corresponding single bonds. This is because the increased binding force causes the two nuclei to be drawn closer together. The single C—C bond has a length of 154 pm in most aliphatic compounds, while the double C=C bond (as in ethene) is shorter at 134 pm, and the triple C $\equiv$ C bond (as in ethyne) is only 120 pm. It is interesting to see how benzene fits

TABLE 2. BOND LENGTHS AND BOND DISSOCIATION ENERGIES

	Bond length (pm)	Bond energy (kJ mol ⁻¹)		(pm)	(kJ mol ⁻¹)
C—C	154	347	C—N	147	305
C=C	134	611	C $\equiv$ N	115	879
C $\equiv$ C	120	813	C—Cl	171	343
C—H	109	413	N—H	101	389
C—O	144	339	O—H	97	460
C=O	120	741	H—H	75	436

into this picture, because the distance between the carbon atoms is found to be 140 pm, which is intermediate between the normal single and double bond lengths. We have seen (p. 37) that the bonding consists of a σ -bond (two shared electrons) plus the π -bond. The latter contains six electrons and is shared by all six carbon-carbon bonds, and therefore averages one electron per bond. There is therefore a total of three electrons shared between each pair of carbon atoms, which is equivalent to one and a half covalent bonds. The actual length of the bond, when compared with the C—C and C=C bond length figures, is equivalent to about one and two-thirds bonds. The additional binding energy is due to the delocalisation of the π -bond, which is shared by all the carbon atoms and is not confined to adjacent atoms. This is one example of the way in which measurements of bond lengths can provide information about the type of bonding in molecules.

Chemical reactions between molecules involve the formation of new bonds and usually the breaking of some of the original bonds, and it is useful to know the amounts of energy involved in these processes. It is possible, from heat measurements, to calculate the mean energy necessary to break a particular type of bond (§ 11.9). The energy required to break a molecule down into its individual atoms is the sum of the *bond dissociation energies* for the various bonds concerned. If the molecule is a simple one (e.g. H₂, CH₄) the separate bond energies are easily found: for example, one quarter of the energy needed to dissociate a methane molecule will be equal to the C—H bond dissociation energy.

Some bond dissociation energies are shown in Table 2. It will be noticed that a double bond is not twice as strong as a single bond. For example, $\text{C}-\text{C}$ gives a value of 347 kJ, but $\text{C}=\text{C}$ is stronger by only 264 kJ, while the third bond in $\text{C}\equiv\text{C}$ adds a further 202 kJ. This is because the bonds are not all of the same type, the single bond being a σ -bond and the double and triple bonds consisting of one σ -bond plus one and two π -bonds respectively. A π -bond is thus weaker than a σ -bond, so that in an unsaturated organic compound (*i.e.* one containing a $\text{C}=\text{C}$ or $\text{C}\equiv\text{C}$ bond) the π -bonds will normally be the weakest bonds present. This explains the high reactivity of unsaturated molecules (*e.g.* ethene and ethyne) where the π -bond is readily broken, while the $\text{C}-\text{C}$ bond that remains is more stable. In benzene the position is different because the π -bonds are continuous around the carbon ring (*i.e.* delocalised) and are therefore more stable. As a result of this the $\text{C}-\text{H}$ bond is the weakest in the benzene molecule, and substitution reactions occur much more readily than addition reactions.

3.6. The metallic bond

Metals in the solid state are good conductors of electricity, a property which distinguishes them from non-metals, ionic compounds and molecular compounds. Electrical conduction is caused by the movement of charged particles under the influence of an electric field, and since the atoms in a solid are not free to move about it must be concluded that metals contain mobile electrons. Another characteristic of metals is their high mechanical strength, which shows that considerable force is required to pull the atoms apart, in other words strong bonds exist between the atoms. Now a study of the crystal structure of metals shows that in most cases each atom has twelve (or sometimes eight) near neighbours, that is, atoms all equidistant from it. It may be concluded from this that each atom is bound to twelve (or eight) other atoms by the same type of bond. Since it is impossible for an atom to take part in this number of ordinary covalent bonds, and taking into account also the special properties of metals, it is evident that the bonds in metals are of a special type, known as *metallic bonds*.

The metallic elements are found on the left of the periodic table, where the number of valence electrons is less than the number of orbitals available to hold them. This makes it possible for an electron to pass from one atom to another through overlapping orbitals. Consider the case of lithium, which has one *s* valence electron. In the solid crystal, each lithium atom is very close to eight other atoms, so that its orbitals will overlap with all of them at the same time (Fig. 14) and this will be continued throughout the crystal. The electrons are shared continuously by all the atoms, that is, they are completely delocalised. Another way of portraying a metal is as a network of ions in a "sea" of electrons, with the electron sea acting as the binding force which holds the metal ions together.

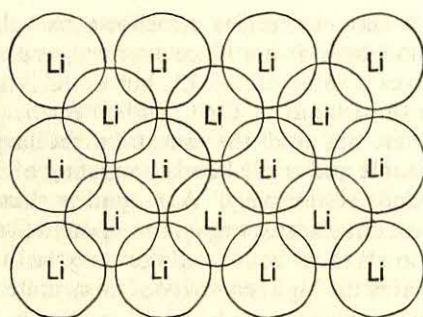


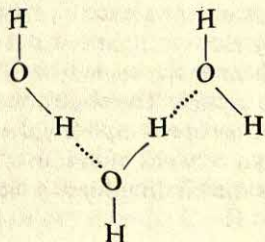
Fig. 14. Metallic bonds

The valence electrons are not associated with any particular atom and can therefore move about: if the two ends of a piece of metal are connected to the poles of a battery, electrons will move towards the positive pole where they will flow out of the metal into the battery, being replaced by fresh electrons from the negative pole. In this way an electric current can pass through the metal.

The number of electrons shared between adjacent atoms is small (in the case of lithium, each atom contributes one-eighth of an electron, so that there is one-quarter of an electron per bond), but the continuous nature of the orbitals (delocalisation of electrons) increases the strength of the bond. There are also many bonds because each atom is bound to many surrounding atoms, so that the total binding energy in metals is high.

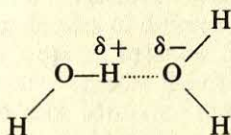
3.7. Hydrogen bonding

Molecules that contain O—H and N—H bonds (*e.g.* water, alcohols, carboxylic acids, phenols, amines, amides) show a strong tendency to *associate*, that is, to link up to form larger molecules. The tendency occurs both in the solid form and in solutions in certain solvents; it can be demonstrated by the observed fact that the relative molecular mass is greater than the normal value. Thus a lower carboxylic acid dissolved in benzene is found to have a relative molecular mass exactly twice the normal value, while the lower alcohols give values increasing up to several times normal as the concentration of the solution increases. Investigation of the crystal structure of ice shows that the molecules are linked in the following way:



Since the hydrogen atom appears to form a linkage between two oxygen atoms, this is known as a *hydrogen bond*. It is impossible for the hydrogen to participate in a second covalent bond, so the additional bond is shown as a dotted line.

Hydrogen bonds are always of the type $\text{—A—H} \cdots \text{B—}$, where A and B may be atoms of either oxygen, nitrogen, fluorine, chlorine or (less commonly) carbon. It is significant that these elements are all more electronegative than hydrogen, so that the A—H bond will be polar with the hydrogen at the negative end. Similarly, the atom B will have a negative charge, so that the main binding force may be regarded as being due to electrostatic attraction:

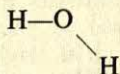


Measurements show that the $\text{—H} \cdots \text{O}$ distance is a little closer than it is possible for a hydrogen and an oxygen atom to approach without overlap of their electron orbitals, so that there appears to be some proportion of covalent bonding in addition, but the exact nature of the hydrogen bond has still to be decided.

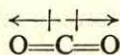
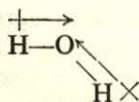
Hydrogen bonds are comparatively weak, with bond energies of $10\text{--}30 \text{ kJ mol}^{-1}$, but they are widespread and have important effects on certain physical properties which will be discussed later.

3.8. Molecular structure

There are various pictorial ways in which information about the structure of molecules can be conveyed. Thus we can give the formula of hydrogen as H_2 , which tells us that the molecule contains two hydrogen atoms, or we can write it H—H , showing the additional fact that the two atoms are linked by a covalent bond. Again, the water molecule may be written as H_2O or H—O—H . The latter formula, however, although showing the types of bond correctly, does not indicate that the molecule is actually not linear. A better description is provided by showing the correct bond angle:

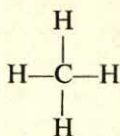


The shape of a molecule often influences its physical properties, for example in a linear molecule the dipole moments of the bonds may cancel each other out and leave the molecule, as a whole, *non-polar*; whereas if the molecule is bent the bond moments will combine to give a resultant moment, so that the molecule is *polar*, as in the following examples:

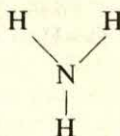
carbon dioxide
(non-polar)water
(polar)

Many physical properties of a material are affected by the polarity of the molecules of which it consists.

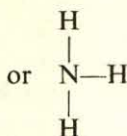
Molecules containing three- and four-valent atoms (*e.g.* nitrogen and carbon) are usually three-dimensional, but in order to show their structural formulae in two dimensions on paper they are conventionally "flattened". Methane and ammonia, for example, may be depicted by the following formulae:



methane (non-polar)

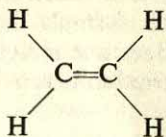


ammonia (polar)



In methane, the four bonds are actually directed outwards in space at equal angles to each other: the bond moments cancel out, and the molecule is non-polar. The bonds in ammonia are at 109° angles and the molecule is in the shape of a pyramid, with the nitrogen at the peak and the hydrogen atoms at the three points of the base: there is a resultant bond moment and the molecule is polar.

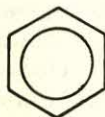
It is less common for molecules to be flat (or more correctly, planar). Examples are ethene, benzene and some of their compounds. The ethene molecule is kept flat by the π -bond, which prevents rotation of the two carbon atoms relative to one another.



ethene



(a)



benzene (b)

The benzene molecule is flat chiefly because of the 120° bond angles, which exactly fit a regular hexagon. It will be noticed that the bond angles in these unsaturated compounds are different from the normal $109\frac{1}{2}^\circ$ tetrahedral angle. This is because the carbon atom is taking part in only three σ -bonds, and these are coplanar at 120° angles. The continuous π -bond in benzene can be shown as illustrated in (b) above,

or the bonding can be shown conventionally as alternate double and single bonds as in (a).

3.9. Relative molecular mass and the mole

The relative mass of a molecule is measured in exactly the same way as relative atomic masses, *i.e.* compared with the mass of the ^{12}C carbon isotope. It follows that *the relative molecular mass of a substance is equal to the sum of the relative atomic masses of all the atoms in the molecule*. It is common to use the same term for ionic compounds, although in this case there is no actual molecule.

The relative molecular mass is not a measure of quantity; it expresses the relative masses of molecules of different substances. When dealing with chemical reactions we want to know the amounts of the different substances which will react, whereas the chemical equation tells us the number of molecules of each substance that take part in the reaction. It is therefore convenient to deal with amounts of different substances in terms of a fixed number of molecules (or atoms, ions, electrons, etc.). For this purpose the *mole* (symbol mol) is defined as *the amount of substance containing the same number of units as there are atoms in 12 g of ^{12}C* . It follows that one mole will have a mass (in grams) equal to either the relative molecular mass, or (in the case of atoms) the relative atomic mass. This applies also to ions, as shown by the following examples:

- 1 mol of CO_2 has a mass of 44.01 g
- 1 mol of NaCl has a mass of 58.44 g
- 1 mol of Na^+ has a mass of 22.99 g
- 1 mol of SO_4^{2-} has a mass of 96.06 g

The actual number of units per mole is equal to 6.023×10^{23} , and is known as the Avogadro constant (symbol L).

QUESTIONS

G.C.E.

1. Explain clearly the terms *electrovalency* and *covalency*, giving two examples in each case. Account for the formation of the tetra-ammonia cupric ion and the compound $\text{NH}_3 \cdot \text{BF}_3$. State the more important physical properties associated with electrovalency and covalency as exemplified by the hydrides, oxides and chlorides of calcium and carbon respectively.

[London

2. How do the atomic structures of the inert gases differ from those of the halogens and the alkali metals? Explain how this difference may be used to account for the tendency of the alkali metals to form only ionic compounds, whilst the halogens form both ionic and covalent compounds. Indicate diagrammatically how the valence electrons are distributed in sodium

chloride, magnesium oxide, carbon tetrachloride and hydrogen chloride. Show how these arrangements are reflected in (a) the electrical conductivity, (b) the volatility, (c) the solubility in water, of the compounds concerned.

[Cambridge]

3. Explain concisely, giving one example in each case, the meaning of (a) atomic mass, (b) atomic number, (c) isotope.

The element of atomic number 17 forms one compound with the element of atomic number 12 and another compound with the element of atomic number 6. Represent by conventional diagrams the electronic structures of the compounds formed and name the type of valency displayed. For each compound state whether you would expect it to be gaseous, liquid or solid and give three other properties which you would expect it to possess.

[J.M.B.]

4. Discuss the following experimental facts in terms of the electronic theory: (a) A solution of hydrogen chloride in dry benzene does not conduct electricity. (b) When fused lithium hydride is electrolysed, hydrogen is evolved at the anode. (c) Few trivalent, and still fewer tetravalent, cations are known in contrast to the many monovalent and divalent cations. (d) The higher the relative atomic mass of an alkali metal, the greater the vigour with which it reacts with water. (e) Boron trifluoride reacts with hydrogen fluoride to give an addition compound HBF_4 , which is a strong acid.

[W.J.E.C.]

5. Explain the characteristics of the different types of bond that occur in chemical compounds. Give a brief account of the bonding in the following: (a) carbon tetrachloride, (b) diamond, (c) ammonium chloride, (d) potassium ferrocyanide, (e) acetic acid dissolved in benzene.

[Cambridge, "S"]

6. Discuss the validity or otherwise of the term *molecule* when applied to the entities commonly formulated as follows: (a) H_2O , (b) AlCl_3 , (c) SiO_2 , (d) NaCl , (e) $\text{NiSO}_4 \cdot 7\text{H}_2\text{O}$.

[W.J.E.C., "S"]

CHAPTER 4

THE KINETIC THEORY OF MATTER

4.1. The states of matter

When the properties of a material are studied it is not the properties of single molecules that are involved, but the properties of aggregates of large numbers of molecules. The behaviour of matter in the bulk depends not only on the nature of individual molecules but also on the effect they have on each other, as well as the conditions (*e.g.* temperature, pressure, etc.) under which they are studied.

All matter may exist in the three states of solid, liquid and gas. A solid is rigid and has a definite shape. A liquid can flow, and so alter its shape, but like a solid it has a definite bounding surface. A gas can also flow but differs from both liquid and solid in that it has no surface, so that it will completely fill any space available to it. Another characteristic property of a gas is that changes in pressure cause marked volume changes. Solids and liquids, on the other hand, are almost incompressible.

The conditions of temperature and pressure decide the state in which a material will exist, and by a suitable change in the conditions it can be transformed from one state to another. Supposing the pressure to be kept the same (normal atmospheric pressure, for example), an increase in temperature may cause a solid to melt and thus become a liquid, while at a still higher temperature the liquid will boil and become vapour* (*i.e.* a gas). Thus water is a solid (ice) below 0°C , melts at the latter temperature to a liquid, and if the temperature is raised to 100°C it boils and becomes a gas (water vapour, or steam). In the process of transition from *solid* $\rightarrow$ *liquid* $\rightarrow$ *gas* there is a continual intake of energy by the material, which may be separated into the following steps:

(a) *Raising the temperature of the solid to the melting point.* The amount of heat that has to be supplied depends on the heat capacity of the material (the *heat capacity* of a system is *the quantity of heat required to raise the temperature by one kelvin*).

(b) *Melting the solid.* During this transition the temperature remains constant, but the solid takes up heat as it melts (the *enthalpy of fusion*).

* The term *vapour* is used to describe a material in the gaseous state when it can be condensed to the liquid form by increasing the pressure at the same temperature. A vapour is therefore a gas below its critical temperature (§ 6.1).

(c) *Raising the temperature of the liquid to the boiling point.* Heat must be supplied according to the heat capacity of the liquid.

(d) *Boiling the liquid.* The temperature remains constant during the transition liquid $\rightarrow$ gas, but the *enthalpy of vaporisation* is taken up.

The whole process can be reversed by cooling the material, *i.e.* by extracting energy from it. When a vapour condenses, or a liquid solidifies, the heat *evolved* is exactly equal to the amount of heat *absorbed* during boiling or melting.

It follows that when a material is in any one state (either solid, liquid or gas) its temperature rises when it absorbs energy, and falls when it loses energy. In other words, temperature is a measure of the amount of energy possessed by the material. We must now consider what forms this energy may take. The quantities of energy involved are usually much smaller than the quanta of the electronic energy levels (it is only at very high temperatures that the electrons in atoms are moved to higher levels, as shown by the spectra emitted by some atoms when strongly heated in a flame). There are, however, various forms of mechanical energy that a molecule may possess. If the molecules can move about, they will have *kinetic energy of motion*; if they can rotate, they will have *rotational energy*; and lastly the atoms in a molecule may vibrate to give *vibrational energy*. Fig. 15 shows rotation and vibration in a diatomic molecule. Since it is the movement of mass that matters, only the nuclei of the two atoms are shown.

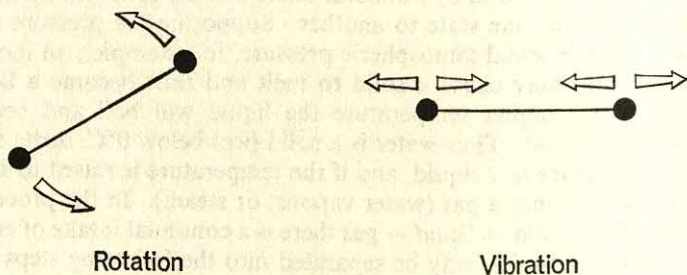


Fig. 15. Rotation and vibration of a diatomic molecule

These three forms of energy have one factor in common: they all involve kinetic energy, which is the energy possessed by bodies in motion. This approach to an explanation of the physical behaviour of matter is therefore called the *kinetic theory*, from the Greek *kinesis* (motion).

A solid has a rigid shape, which suggests that the molecules are not able to move about: it is, in fact, known that they can only vibrate. Liquids and gases, on the other hand, flow readily and also show the property of *diffusion*. The latter phenomenon can best be explained by a simple illustration. If a gas tap is left open for a few seconds, a smell

of gas is quickly noticed some distance away, showing that the gas molecules have dispersed and mixed with the surrounding molecules of air. This rapid diffusion can only be explained by assuming that the molecules of a gas are in constant and rapid motion. Diffusion also occurs in liquids, but much more slowly because the closer packing of the molecules hinders motion. The first direct evidence that molecules are in constant motion was obtained by Robert Brown in 1827, when he observed that grains of pollen suspended in water were in a continual state of agitation (the *Brownian movement*), owing to bombardment by water molecules.

4.2. Intermolecular forces

The two chief similarities between solids and liquids are that they are almost incompressible and that both have a definite surface. The first point suggests that the molecules are practically touching, so that it is impossible to force them much closer together even when a high pressure is applied. It may seem strange at first sight that the molecule, with its rather nebulous clouds of electrons, should behave in this way like a hard and solid object. The reason is that the outer (valence) electrons are all in filled orbitals as a result of electron-pairing during bond formation. These filled orbitals cannot overlap with the orbitals of other molecules, so that when two molecules approach each other closely strong repulsive forces are encountered. For the purposes of the kinetic theory, we can regard molecules as solid objects of definite size.

The existence of a surface in solids and liquids indicates that there are strong forces holding the molecules together, so that they cannot easily break away (some manage to escape in the form of vapour, but this will be disregarded for the time being). These are the forces of intermolecular attraction, sometimes called van der Waals forces, which operate between any molecules that approach within a certain distance of each other.

The van der Waals forces are electrical in nature. To see how they arise, it will be easier to consider first how there can be attraction between molecules that are polar. Fig. 16(a) shows how electrical attraction can occur when oppositely charged poles of a polar molecule are close together. The electrical field of the dipoles also causes an additional induced moment in adjacent molecules, thus increasing the attractive force. It is more difficult to understand why non-polar molecules, and even single atoms, should attract one another. That such forces do exist is demonstrated by the fact that all substances, at a low enough temperature, become solid. The explanation is that these forces, too, are due to dipole attractions. The dipoles are produced by oscillation of the nuclei and electron clouds of atoms with respect to one another, so that at any particular instant the atom may be polar. If the oscillations in adjacent atoms are in phase, there will be attraction, as shown in Fig. 16(b). This type of force is small in the case of atoms

and small molecules, but it increases, in general, with the size of the molecule.

The effect of intermolecular forces depends critically on the distance between molecules, because the forces are only effective over short distances. An idea of the average distance between molecules in the different states of matter can be obtained by comparing the densities of the same substance in the solid, liquid and gaseous forms. The density of a liquid is usually a little lower than that of the corresponding solid: if the molecules are assumed to be touching in the solid, then in the liquid they must still be close together, and in both states they will be subject to intermolecular forces all the time. A gas at ordinary pressures has a very low density compared with the liquid or solid forms, so that the molecules are usually too far apart for the attractive forces to

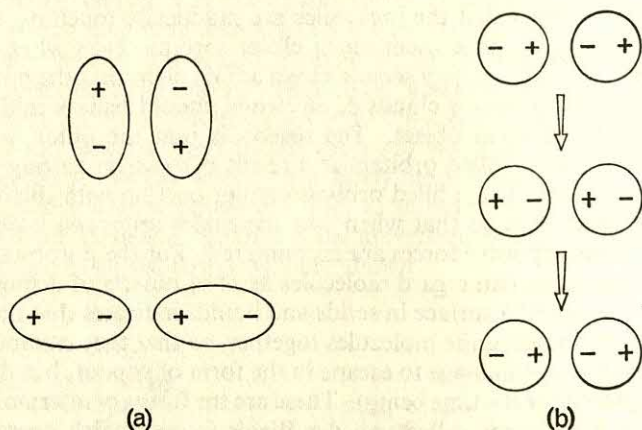


Fig. 16. Forces of intermolecular attraction between (a) polar molecules, (b) atoms and non-polar molecules

operate. Fig. 17 shows approximately how the distances compare in the three states of matter. It must be remembered that these are *average* distances: the molecules in a gas will not always be so far apart, because they are in constant motion at high speeds and their paths will frequently bring them close together or into collision with one another.

We will now consider the transition *solid* $\rightarrow$ *liquid* $\rightarrow$ *gas* in the light of the following facts:

(a) The intermolecular forces will tend to pull the molecules close together.

(b) The kinetic energy of the molecules will tend to keep them in motion, and so move them apart.

(c) The kinetic energy increases as the temperature rises.

(d) The molecules are very close together in a solid, a little farther apart in a liquid, and very far apart (on average) in a gas.

When a solid melts, the molecules move apart against the pull of the van der Waals forces. This can only occur when the molecules have sufficient energy to overcome the attractive forces, so that melting occurs when the temperature reaches a certain definite value, which is the melting point. As the molecules move apart, work is being done ($\text{Work} = \text{Force} \times \text{Distance moved}$) so that the energy of the molecules will fall unless energy (the enthalpy of fusion) is supplied. The transition *liquid* $\rightarrow$ *gas* occurs at a higher temperature (the boiling point) where the kinetic energy is high enough for the molecules to overcome the attractive forces completely. The molecules now move far apart, and the energy required (the enthalpy of vaporisation) is usually greater than the enthalpy of fusion.

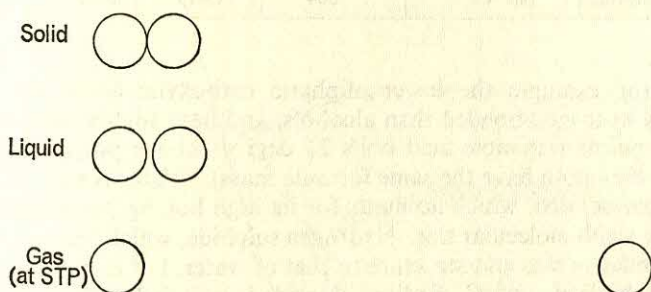


Fig. 17. Average distances between molecules in the three states of matter

In ionic compounds there are attractive forces between the oppositely charged ions: these are called *interionic forces*. They are stronger than the van der Waals forces, partly because the charge carried by an ion is larger than that of a molecular dipole and partly because an ion attracts all ions of opposite charge that are near it, whereas dipoles cause attraction only when the molecules are orientated in certain directions (*see* Fig. 16).

Melting and boiling points represent a state of balance between the kinetic energy of the molecules and the intermolecular or interionic forces. It is therefore to be expected that substances with weak attractive forces will melt and boil at lower temperatures than those with strong forces. The figures given in Table 3 illustrate this point. The first set of figures refers to normal aliphatic hydrocarbons of increasing relative molecular mass, and shows how the melting and boiling points both increase with molecular size. The next group contains substances of roughly the same molecular size (ethane, methoxymethane and ethanol) and shows: (a) the increase in melting and boiling points caused by the stronger intermolecular forces between polar molecules as compared with non-polar (methoxymethane and ethane); and (b) the additional effect of hydrogen-bonding, as in ethanol, with an even higher boiling point. The stronger the hydrogen-bonding, the greater will be the latter

TABLE 3. MELTING POINTS AND BOILING POINTS

<i>Substance</i>	<i>Formula</i>	<i>Melting point (°C)</i>	<i>Boiling point (°C)</i>	<i>Molecular type</i>
butane	C ₄ H ₁₀	-135	-1	} non-polar
pentane	C ₅ H ₁₂	-130	36	
hexane	C ₆ H ₁₄	-94	69	
heptane	C ₇ H ₁₆	-90	98	
ethane	C ₂ H ₆	-172	-88	non-polar
methoxy- methane	CH ₃ OCH ₃	-139	-24	polar
ethanol	C ₂ H ₅ OH	-115	78	polar and hydro- gen-bonded
sodium chloride	Na ⁺ Cl ⁻	804	1,410	ionic

effect, for example the lower aliphatic carboxylic acids are more strongly hydrogen-bonded than alcohols, and have higher melting and boiling points (ethanoic acid boils 21 degrees above propan-1-ol, although they both have the same formula mass). Water is very strongly hydrogen-bonded, which accounts for its high boiling point compared with the small molecular size. Hydrogen sulphide, which has a molecule very similar in size and structure to that of water, but is not hydrogen-bonded, boils at -62°C . Sodium chloride is included in the table as an example of an ionic compound. Its very high melting and boiling points indicate the strength of interionic forces compared with the van der Waals forces.

4.3. The distribution of energy among molecules

One fact that follows from the kinetic theory is that the molecules in a particular system cannot all have the same energy. Consider the molecules in a gas or a liquid. Since they are all moving at random, they will be continually colliding with each other. In each collision there will be an interchange of momentum (Momentum = Mass $\times$ Velocity) with the result that the velocity of both molecules involved in the collision will alter. A change in velocity means a change in energy (kinetic energy = $mu^2/2$, where m is the mass and u the velocity), so that collisions cause an interchange of energy between molecules. The total energy of the system must remain constant, but the energy of an individual molecule will be continually changing.

The way in which the total energy of a collection of molecules is distributed among the individual molecules is a statistical problem which was first solved by Maxwell in 1860 for the case of a gas. The result can be shown in the form of a probability curve (Fig. 18), in which one axis is used to show the kinetic energy, while along the other axis is plotted the proportion of the total number of molecules that have any particular energy value. The peak of the curve corresponds with

the most probable energy value, while on either side there are decreasing numbers of molecules with energies either higher or lower than this value. The dotted curve shows what happens if the temperature is raised. The maximum of the curve moves to a higher energy value, showing the general increase of kinetic energy with temperature, and at the same time the curve broadens out so that there is a greater proportion of molecules with energies much higher than the average.

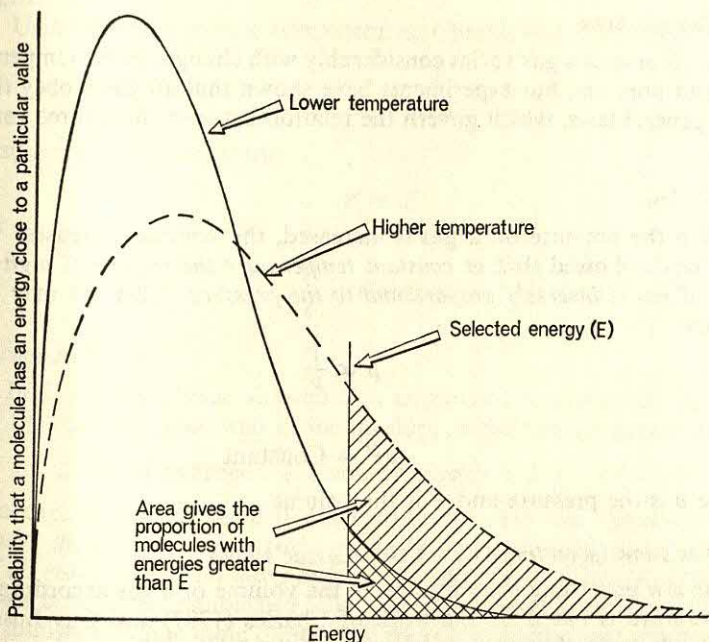


Fig. 18. Distribution of energies among gaseous molecules at different temperatures

Molecules with high energies are of particular interest in many physical and chemical problems. To take one example, in a liquid below its boiling point there are always some molecules with sufficient energy to break away from the intermolecular forces, thus causing evaporation. This requires a definite amount of energy, so that it is useful to know what proportion of the molecules have an energy greater than a certain value. This can be found from the area under the energy distribution curve, measured from the required energy value upwards as shown by the shaded areas in Fig. 18. Note how this proportion increases as the temperature is raised.

CHAPTER 5

GASES

5.1. The gas laws

The volume of a gas varies considerably with changes in the temperature and pressure, but experiments have shown that all gases obey the same general laws, which govern the relation between these three variables.

Boyle's law

When the pressure on a gas is increased, the volume decreases. In 1662 Boyle showed that *at constant temperature the volume of a given mass of gas is inversely proportional to the pressure*. This law may be written:

$$p \propto \frac{1}{V}$$

or

$$pV = \text{Constant}$$

where p is the pressure and V is the volume.

Charles's law (sometimes called Gay-Lussac's law)

The law governing the variation in the volume of a gas according to temperature is based on the work of Charles (1787) and Gay-Lussac (1802). It states that *at constant pressure the volume of a gas increases by $\frac{1}{273}$ of its volume at 0°C for every degree rise in temperature*. If a given mass of gas has a volume V_0 at 0°C , then the volume at $t^{\circ}\text{C}$ and the same pressure will be given by the equation:

$$\begin{aligned} V_t &= V_0 + t \frac{V_0}{273} \\ &= V_0 \frac{t + 273}{273} \end{aligned}$$

The discovery of this relationship led to the adoption of what is now known as the *thermodynamic temperature* scale (see p. 299). The unit of temperature is the kelvin (symbol K), and is used both for a temperature interval (identical with the degree Celsius), and to denote the actual temperature. Thermodynamic temperatures are denoted by the symbol T . As many equations involve temperatures on the thermodynamic scale, care must be taken in calculations to see that temperatures

measured as $t^{\circ}\text{C}$ are converted to kelvin, where necessary, by adding 273:

$$T = t + 273$$

There are theoretical reasons for believing that it is impossible to achieve a temperature lower than the absolute zero (0 K). The lowest temperature that has been reached is extremely close to the absolute zero.

Using thermodynamic temperatures, Charles's law becomes:

$$V = V_0 \frac{T}{273}$$

and since V_0 is a constant:

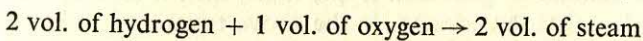
$$V \propto T$$

or

$$\frac{V}{T} = \text{Constant}$$

Avogadro's law

In 1808 Gay-Lussac showed that in gaseous reactions the volumes of the reacting gases, and of the products, were simply related, *e.g.*:



To explain this, Avogadro put forward in 1811 the hypothesis that *under the same conditions of temperature and pressure, equal volumes of all gases contain the same number of molecules*. The truth of this has since been firmly established, and it is now known as Avogadro's law. It follows that one mole of any gas, measured at the same temperature and pressure will have the same volume.

The volume occupied by one mole of gas, *i.e.* the *molar volume*, will depend on the temperature and pressure. Volumes of gas are often given for a standard temperature and pressure (written STP) which is usually taken as 0°C and 101.3 kPa (equal to 760 mm of mercury; see p. 300 for the derivation of pressure units). The molar volume of a gas at STP is 22.4 dm^3 .

5.2. The ideal gas equation

The gas laws can be combined to give a single equation in the following way. Suppose a given mass of gas to have a volume V_1 at a pressure p_1 and temperature T_1 . If the pressure is now changed to p_2 , keeping the temperature constant, and the new volume is V , then from Boyle's law:

$$p_1 V_1 = p_2 V$$

Suppose the pressure now to be kept constant at p_2 while the temperature is altered to T_2 , the final volume being V_2 . Then from Charles's law:

$$\frac{V}{T_1} = \frac{V_2}{T_2}$$

or

$$V = \frac{V_2 T_1}{T_2}$$

Substituting for V in the first equation:

$$p_1 V_1 = \frac{p_2 V_2 T_1}{T_2}$$

or

$$\frac{p_1 V_1}{T_1} = \frac{p_2 V_2}{T_2}$$

It follows that for a given mass of gas, under any conditions of temperature, pressure and volume, we can write:

$$\frac{pV}{T} = \text{Constant}$$

If the amount of gas taken is one mole, then it follows from Avogadro's law that the constant in the above equation will be the same for all gases. The equation may therefore be written

$$pV = nRT$$

where V is the volume containing n mole of gas, and R is a universal constant, called the *gas constant*.

Although many gases (e.g. hydrogen, oxygen and nitrogen) obey the gas laws reasonably well at ordinary temperatures and pressures, all gases show some deviation from these laws. We say, therefore, that the gas laws are only obeyed exactly by a hypothetical *ideal gas*, and the above equation is known as the *ideal gas equation*. For actual gases, corrections are applied, where necessary, to allow for their departure from ideal behaviour.

The value of the gas constant can be calculated from the fact that 1 mole of gas occupies 0.0224 m^3 at 0°C and $101\,300 \text{ Pa}$ pressure:

$$\begin{aligned} R &= \frac{pV}{T} = \frac{101\,300 \times 0.0224}{0 + 273} \\ &\approx 8.31 \text{ Nm K}^{-1} \text{ mol}^{-1} (= \text{J K}^{-1} \text{ mol}^{-1}) \end{aligned}$$

Note that, since newtons $\times$ metres (force $\times$ distance) represents energy, R is in energy units ($\text{Nm} = \text{J}$).

The ideal gas equation can be used to calculate the volume that a given mass of any gas will occupy under specified conditions of temperature and pressure.

EXAMPLE

What volume would be occupied by 100 g of oxygen at 18°C and 105 kPa pressure? (O = 16).

$$n = \frac{100}{32} \text{ mol} \quad T = 18 + 273 = 291 \text{ K} \quad pV = nRT$$

$$V = \frac{nRT}{p} = \frac{100 \times 8.31 \times 291}{32 \times 105 \times 10^3} = 0.0720 \text{ m}^3$$

It is sometimes necessary to convert the volume of a gas, measured at a certain temperature and pressure, to the volume that the gas would occupy under different conditions (e.g. STP). This is done by using the relationship

$$\frac{p_1 V_1}{T_1} = \frac{p_2 V_2}{T_2}$$

or

$$V_2 = V_1 \frac{p_1 T_2}{p_2 T_1}$$

EXAMPLE

A gas occupies a volume of 136 cm³ at 21°C and 102 kPa. What would its volume be at STP?

$$\begin{aligned} V &= 136 \times \frac{102 \times 273}{101.3 \times 294} \\ &= 127 \text{ cm}^3 \end{aligned}$$

Note that any units may be used for the pressures, as long as both are in the same units. Temperatures must always be in kelvin.

5.3. Gas mixtures

In a mixture, the total pressure is made up of the individual pressures exerted by all the gases present. *Dalton's law of partial pressures* (1801) states that *the total pressure of a mixture of gases is equal to the sum of the partial pressures of the constituents*. The *partial pressure* of each gas is *the pressure it would exert if it alone occupied the same volume as the whole mixture*.

Thus if a mixture consists of two gases with partial pressures p_1 and p_2 , the total pressure will be:

$$p = p_1 + p_2$$

The partial pressures can be calculated from the amounts of the individual gases present. Suppose that these are n_1 and n_2 moles respectively. If the volume occupied by the mixture is V , then if the first gas alone occupied this volume its pressure would be given by the gas equation as:

$$p_1 V = n_1 RT$$

For the whole mixture the total number of moles is $n_1 + n_2$, and the pressure is p , so that:

$$pV = (n_1 + n_2)RT$$

Dividing this equation into the one above:

$$\frac{p_1}{p} = \frac{n_1}{n_1 + n_2}$$

The fraction $n_1/(n_1 + n_2)$ is equal to the number of moles of gas (1) divided by the total number of moles present; this is called the *mole fraction*, written x_1 . The partial pressures can thus be calculated in the following way:

$$\begin{aligned} p_1 &= p \frac{n_1}{n_1 + n_2} \\ &= px_1 \end{aligned}$$

and similarly

$$p_2 = px_2$$

Another application of partial pressures occurs in the measurement of volumes of gas that have been collected over water. Owing to the vapour pressure of water, what is measured is actually the volume of a mixture of the gas and water vapour. The partial pressure of the water vapour will be equal to the vapour pressure of water at the temperature at which the collection was made, and this can be found from tables. The volume of dry gas can then be calculated.

EXAMPLE

The volume of a gas, measured over water at 19°C and 99.7 kPa pressure, was 207 cm³. What is the volume of dry gas at STP?

The vapour pressure of water at 19°C is 2.3 kPa. The partial pressure of the dry gas p can be found from Dalton's law:

$$\begin{aligned} 99.7 &= p + 2.3 \\ p &= 97.4 \text{ kPa} \end{aligned}$$

The dry gas would therefore occupy a volume of 207 cm³ at 19°C and 97.4 kPa. The correction to STP can now be made in the usual way:

$$\begin{aligned} V &= 207 \times \frac{97.4 \times 273}{101.3 \times 292} \\ &= 186 \text{ cm}^3 \end{aligned}$$

5.4. Gaseous diffusion

The phenomenon of diffusion has already been described (§ 4.1). Gases diffuse rapidly, because of the rapid motion of the molecules and the large distances between them. If two gases are put into the same container, they will mix completely after a short time. As well as spreading throughout the space available to them, gases also diffuse through porous membranes, such as a porous pot.

Light gases diffuse more rapidly than those with heavier molecules, and in 1833 Graham established the relationship known as *Graham's law of diffusion*: *the rates of diffusion of different gases are inversely proportional to the square roots of their densities*. Thus if the rates of diffusion of two gases, having densities ρ_1 and ρ_2 , are represented by their diffusion coefficients D_1 and D_2 , then:

$$\frac{D_1}{D_2} = \sqrt{\frac{\rho_2}{\rho_1}}$$

Since one mole of any gas occupies the same volume under the same conditions of temperature and pressure, gas densities are proportional to the mass of the mole, *i.e.* to the relative molecular mass. Hence for two gases of relative molecular mass M_1 and M_2 , Graham's law becomes:

$$\frac{D_1}{D_2} = \sqrt{\frac{M_2}{M_1}}$$

Relative molecular masses have been determined in the past by comparing the rate of diffusion with that of a gas of known relative molecular mass. A more important application is in the separation of isotopes. Aston first used this method in 1913 to separate the isotopes of neon, while more recently it has been applied to the large-scale separation of the uranium isotope ^{235}U by repeated diffusion of uranium hexafluoride, which is gaseous at 60°C .

5.5. The kinetic theory of gases

Providing the pressure is not too high, gases obey the gas equation irrespective of the nature of the molecules of which the gas is composed. No such general law applies to solids or liquids. The comparative simplicity of the gaseous state arises from the large distances between the molecules, as a result of which both the intermolecular forces and the actual sizes of the molecules are relatively unimportant. By making some simplifying assumptions, the following definition gives a description of what we may call an *ideal gas*, on which a kinetic treatment may be based:

- (a) A gas consists of a large number of small particles (molecules) in constant motion at random.

(b) The molecules will frequently collide with each other and with the walls of the containing vessel. The collisions must be elastic, *i.e.* no momentum is lost, otherwise the molecules would slow down and eventually stop.

(c) The mean kinetic energy of the molecules remains constant at any one temperature.

(d) There are no intermolecular forces.

(e) The molecules have no volume.

When molecules strike the walls of the vessel in which they are contained, each impact causes a force to be exerted on the wall, giving rise to a pressure over the whole surface. If the volume were decreased, each molecule would strike the walls more frequently, thus increasing the pressure. A rise in temperature would increase the speed of the molecules, and also increase the pressure. These deductions are qualitatively in agreement with the gas laws, but the following treatment will show how the behaviour of our hypothetical ideal gas can be derived quantitatively.

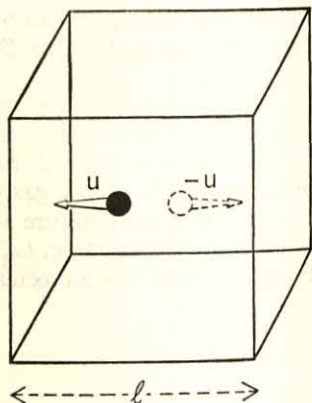


Fig. 19. A molecule rebounding after striking a wall of the container

Suppose a cube of side l m to contain N molecules each having a mass of m kg. Consider a molecule moving parallel with one side of the cube, with a velocity of u m per second (Fig. 19). When the molecule strikes the wall, it will rebound with a velocity of the same magnitude, but in the opposite direction, *i.e.* $-u$. The momentum of the molecule is mu before impact and $-mu$ after impact, so that there has been a change in momentum equal to $2mu$. When the molecule strikes the opposite wall, it will return along the same path, and having travelled a distance of $2l$ m it will strike the first wall again, the interval between the impacts being $2l/u$ seconds.

The number of impacts per second is the reciprocal of this (*i.e.* $u/2l$), and if this is multiplied by the change in momentum for each impact the rate of change of momentum is obtained:

$$\begin{aligned} \text{Rate of change of momentum} &= 2mu \times \frac{u}{2l} \\ &= \frac{mu^2}{l} \text{ kg m s}^{-2} (= \text{N}) \end{aligned}$$

The rate of change of momentum is equal to the force (in newtons) exerted on the wall by the molecule.

The molecules are moving in random directions and with different velocities, but the problem may be simplified in the following way. Since all directions of motion are equally probable, it will be assumed that one-third of the molecules are moving in each of three directions at right angles, parallel with the sides of the cube. The force on one wall is then caused by the impact of $N/3$ molecules. The differences in velocity may be allowed for by substituting the mean square velocity ($\overline{u^2}$) for u^2 :

$$\text{Force on each wall} = \frac{N}{3} \times \frac{m\overline{u^2}}{l}$$

Pressure is equal to force per unit area, and the area of each wall is l^2 , so that:

$$\begin{aligned} p &= \frac{N}{3} \times \frac{m\overline{u^2}}{l} \times \frac{1}{l^2} \\ &= \frac{Nm\overline{u^2}}{3l^3} \text{ N m}^{-2} \end{aligned}$$

Since the volume of the cube (V) is equal to l^3 :

$$p = \frac{Nm\overline{u^2}}{3V}$$

or

$$pV = \frac{1}{3}Nm\overline{u^2}$$

The kinetic energy of a particle of mass m moving with a velocity u is equal to $mu^2/2$, so that the mean kinetic energy of the molecules is $m\overline{u^2}/2$. Comparing this with the last equation, it is seen that:

$$pV = \frac{2}{3}N \times \text{Mean kinetic energy}$$

It has already been shown that the temperature is a measure of the mean kinetic energy of the molecules. If it is now assumed that the kinetic energy is proportional to the thermodynamic temperature, then:

$$pV \propto NT$$

For a given mass of gas (*i.e.* N constant), this becomes $pV \propto T$, so that at constant temperature $pV = \text{Constant}$ (Boyle's law), while at constant pressure $V \propto T$ (Charles's law). At constant temperature and pressure, $V \propto N$, and since no assumption has been made as to the nature of the molecules the proportionality constant will be the same for all gases. Hence equal volumes of all gases will contain the same number of molecules (Avogadro's law).

For one mole of any gas, therefore, N will be constant, and we may rewrite the expression $pV \propto NT$ by putting in a proportionality constant R , so that it becomes

$$pV = RT$$

where the constant R has been chosen to apply to one mole of gas. The expression we have arrived at is now identical with the ideal gas equation.

Graham's law may also be deduced from the kinetic theory. The rate at which molecules diffuse will be proportional to their mean velocity; the latter can be found from the equation deduced above:

$$pV = \frac{1}{3} Nm\bar{u}^2$$

on rearrangement

$$\bar{u}^2 = \frac{3pV}{Nm}$$

If V is made the volume containing one mole of gas, then the total mass of gas (Nm) is equal to the relative molecular mass M in grams, or $M/1000$ kg, so that

$$\bar{u}^2 = \frac{3000 pV}{M}$$

and since $pV = RT$ for one mole of an ideal gas,

$$\bar{u}^2 = \frac{3000 RT}{M}$$

or

$$\sqrt{\bar{u}^2} = \sqrt{\frac{3000 RT}{M}}$$

where $\sqrt{\bar{u}^2}$ is the *root mean square velocity*; this is not quite the same as the mean velocity, but is proportional to it. For two gases at the same temperature, the rates of diffusion will therefore be inversely proportional to the square roots of their molecular masses. If the gases are also at the same pressure, their densities will be proportional to the relative molecular masses, so that the predicted relationship between diffusion and density is in agreement with Graham's law.

The above equation can be used to calculate the root mean square velocities of molecules: thus for oxygen at 0°C :

$$\begin{aligned}\sqrt{\bar{u}^2} &= \sqrt{\frac{3000 \times 8.31 \times 273}{32}} \\ &= 461 \text{ m s}^{-1}\end{aligned}$$

5.6. Deviations from the ideal gas equation

It was discovered as early as 1881 that Boyle's law was not accurately obeyed, especially at high pressures. A convenient way of showing the deviation of gases from ideal behaviour is to plot pV/RT against the pressure (Fig. 20). For an ideal gas, $pV = RT$ and so pV/RT is equal

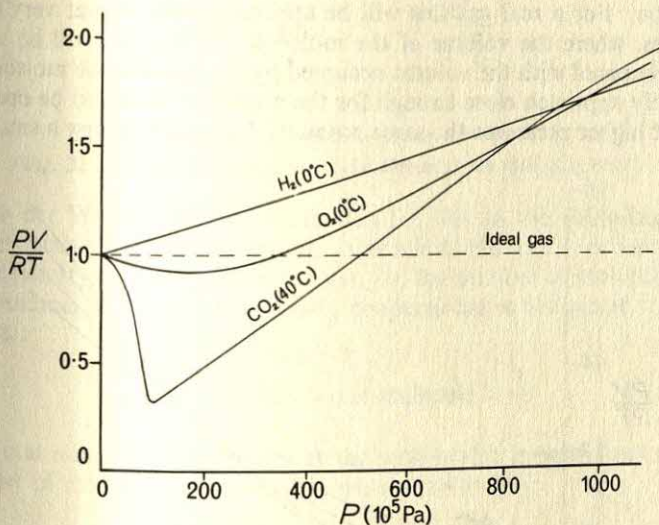


Fig. 20. Deviation of gases from ideal behaviour at high pressures

to one at any pressure, but the curves show that this is far from the case for actual gases. It will be seen that the curves have the following characteristics:

- (a) All the curves approach the same (ideal) value as the pressure approaches zero, i.e. *at low pressures all gases behave as ideal gases.*
- (b) At moderate pressures, there is a negative, or *underperfect*, deviation. Hydrogen does not appear to show it, but this is because the temperature is too high. At a much lower temperature hydrogen gives a curve of the same type as the other gases.
- (c) At very high pressures, there is a positive, or *overperfect*, deviation.
- (d) At high pressures, gases do not even approximately obey Boyle's law.

If the temperature is changed, the shape of the curve remains the same but the deviations become more pronounced as the temperature falls (Fig. 21). The extent of underperfect behaviour actually depends on how near the gas is to the temperature at which it will liquefy: this explains why, in Fig. 20, carbon dioxide shows much greater deviation

than nitrogen, while hydrogen (which liquefies at a much lower temperature than nitrogen) shows no underperfect behaviour.

The fact that actual gases deviate from the ideal gas laws is not unexpected, since the derivation of these laws from the kinetic theory is based on a hypothetical ideal gas, which by definition is assumed to consist of molecules of negligible volume and having no intermolecular attraction. For a real gas this will be approximately true at very low pressures, where the volume of the molecules themselves will be very small compared with the volume occupied by the gas and the molecules will rarely approach close enough for the attractive forces to be operative. At higher pressures the same amount of gas will occupy a smaller

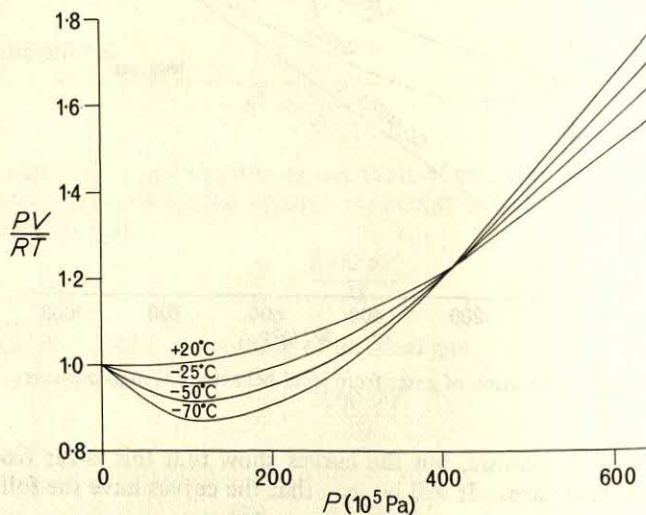


Fig. 21. Non-ideal behaviour of nitrogen at different temperatures

volume, so that the volume of the molecules will become more important; while the molecules will also collide more frequently, so that the intermolecular forces will have greater effect.

In 1873, van der Waals applied corrections to the ideal gas equation to make allowance for (a) the intermolecular attraction, and (b) the volume of the molecules themselves.

Deviation due to intermolecular forces

Each molecule in the bulk of the gas is subject to attractive forces due to the molecules surrounding it in all directions, and so there will be no resultant force acting on it (Fig. 22, molecule A). A molecule close to the wall (molecule B) has attraction on one side only, so that there is a resultant force tending to pull it away from the wall. When a molecule is about to strike the wall, this inward pull acts so as to reduce

the force exerted by the impact and therefore to reduce the pressure exerted by the gas. The observed pressure is thus less than would be expected from the kinetic theory. This will tend to make pV less than RT and so will tend to cause underperfect deviation.

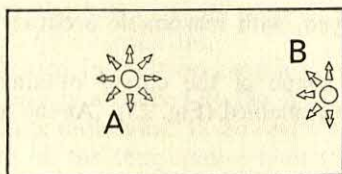


Fig. 22. Inward attraction on molecules near the wall of a vessel

Van der Waals applied a correction for this in the following way. The attractive force acting on one molecule at the wall is proportional to the density of molecules in the gas, *i.e.* the number of molecules per unit volume. The latter is inversely proportional to the molar volume, so that:

$$\text{Force acting on one molecule} \propto \frac{1}{V}$$

The total number of molecules at the wall is also proportional to the number of molecules per unit volume, and so to $1/V$:

$$\text{Number of molecules at wall} \propto \frac{1}{V}$$

hence

$$\begin{aligned} \text{Total attractive force} &\propto \frac{1}{V} \times \frac{1}{V} \\ &\propto \frac{1}{V^2} \end{aligned}$$

$$\text{Corrected pressure} = p + \frac{a}{V^2}$$

where a is a constant for any particular gas.

Deviation due to the volume of the molecules themselves

The volume available for the molecules to move about in is always less than the observed volume because of the space occupied by the molecules themselves. This tends to make pV greater than RT , and can thus give rise to overperfect behaviour. Van der Waals allowed for this by subtracting a correction term from the observed volume.

$$\text{Corrected volume} = V - b$$

where b is a second constant, depending only on the nature of the gas.

If the corrected pressure and volume are introduced into the ideal gas equation in place of p and V , the result is the *van der Waals equation*:

$$\left(p + \frac{a}{V^2}\right)(V - b) = RT$$

This equation is obeyed, with reasonable accuracy, up to quite high pressures.

The characteristic shape of the curves obtained by plotting PV against P can now be explained (Fig. 23). At the lower pressures, the

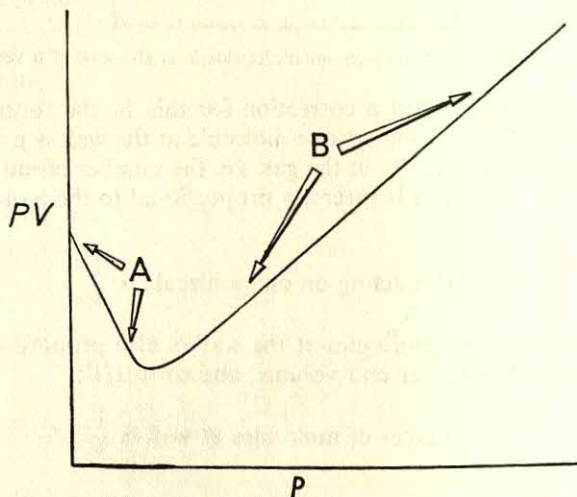


Fig. 23. Underperfect behaviour (A) due to intermolecular attraction, and overperfect behaviour (B) due to the size of the molecules

gas has a large volume, and the volume taken up by the molecules is relatively unimportant, so that the attractive forces cause underperfect behaviour (section A of the curve). As the volume decreases, the size of the molecules becomes more important and eventually predominates, giving overperfect behaviour (section B of the curve).

Measurements of gas volumes are often carried out at atmospheric pressure and room temperature, as for example in gas analysis. For many gases the deviation from ideal behaviour under these conditions is small and may be neglected. To illustrate the magnitude of the resulting inaccuracy, the following figures show the actual molar volumes of some common gases, measured at STP:

Ideal gas	Hydrogen	Nitrogen	Oxygen	Carbon dioxide	Ammonia
22.41	22.43	22.41	22.39	22.26	22.08 dm ³

5.7. The heat capacities of gases

The *heat capacity* of a substance is defined as the quantity of heat required to raise the temperature of one mole of the substance by one kelvin. The units are therefore $\text{J K}^{-1} \text{mol}^{-1}$. When the substance is in the gaseous state, the heat capacity depends also on the conditions under which the heating is carried out.

When a gas is heated in a closed container, so that the volume is kept constant, the energy absorbed by the gas is equal to the increase in kinetic energy of the molecules. If, however, it is the pressure that is kept constant, then as the temperature rises the gas will expand in accordance with Charles's law and will do work against the applied pressure; an additional amount of energy will therefore be absorbed equal to the work done. It is therefore necessary to distinguish between the heat capacity measured at constant volume (C_V), and at constant pressure (C_p). C_p will be greater than C_V by an amount equal to the work done in expansion.

To find the work of expansion, suppose that one mole of gas is enclosed in a cylinder (Fig. 24) of cross-section A , and that a constant

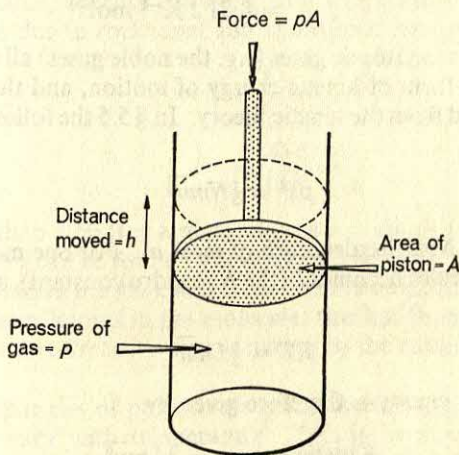


Fig. 24. Work done by the expansion of a gas

force is applied to the piston so that the pressure of the gas is a constant value p . If the piston is moved through a distance h when the gas expands, the work done is given by:

$$\begin{aligned}\text{Work done} &= \text{Force} \times \text{Distance moved} \\ &= pA \times h\end{aligned}$$

Now $A \times h$ is equal to the increase in volume; if the original volume was V we can call this δV . Then:

$$\text{Work done} = p\delta V$$

For the heat capacity, we require the temperature to be raised by one kelvin, from say T to $(T + 1)$. Applying the ideal gas equation to the gas before expansion, we have

$$pV = RT$$

and after expansion

$$p(V + \delta V) = R(T + 1)$$

so that by subtraction

$$p\delta V = R$$

so that the work done in expansion is equal to R . Hence

$$C_p = C_v + R$$

or

$$\begin{aligned} C_p - C_v &= R \\ &= 8.31 \text{ J K}^{-1} \text{ mol}^{-1} \end{aligned}$$

In the case of monatomic gases (*e.g.* the noble gases) all the molecular energy is in the form of kinetic energy of motion, and the value of C_v can be calculated from the kinetic theory. In § 5.5 the following equation was derived

$$pV = \frac{1}{3}Nmu^2$$

where there are N molecules, each of mass m . For one mole of gas, the number of molecules becomes L (the Avogadro constant), and $pV = RT$, so that

$$RT = \frac{1}{3}Lmu^2$$

the total kinetic energy is therefore given by

$$\begin{aligned} \text{Kinetic energy} &= \frac{1}{2}Lmu^2 \\ &= \frac{3}{2}RT \end{aligned}$$

If the temperature is increased by one kelvin, the kinetic energy increases by

$$\begin{aligned} \frac{3}{2}R(T + 1) - \frac{3}{2}RT &= \frac{3}{2}R \\ &= 12.5 \text{ J K}^{-1} \text{ mol}^{-1} \end{aligned}$$

so that this quantity is equal to the heat capacity at constant volume:

$$C_v = 12.5 \text{ J K}^{-1} \text{ mol}^{-1}$$

and

$$\begin{aligned}C_p &= C_V + 8.3 \\ &= 20.8 \text{ J K}^{-1} \text{ mol}^{-1}\end{aligned}$$

The ratio of the two heat capacities (γ) will be:

$$\begin{aligned}\gamma &= \frac{C_p}{C_V} \\ &= 1.66\end{aligned}$$

This value is in agreement with that found in practice for monatomic gases, such as the noble gases and some other elements in the gaseous state (*e.g.* mercury).

Molecules that contain more than one atom have rotational and vibrational energy in addition to kinetic energy of motion (§ 4.1). Part of the energy supplied is now used to increase the amounts of these other forms of energy, so that the heat capacity of a polyatomic gas is greater than that of a monatomic gas by an amount depending on the complexity of the molecule. The difference between C_p and C_V remains the same, because the work done in expansion is not affected. If the increase due to rotational and vibrational energy is x , then

$$\begin{aligned}\gamma &= \frac{C_p}{C_V} \\ &= \frac{20.8 + x}{12.5 + x}\end{aligned}$$

which is less than 1.66 (for a diatomic gas γ is about 1.4).

The value of γ can be found by several methods (*e.g.* by measuring the velocity of sound in the gas), and is useful in determining the atomicity, *i.e.* the number of atoms in the molecule: this has found application in the determination of relative atomic masses by the method of gas density (§ 2.7).

The heat capacities of polyatomic gases (atomicity greater than one) are found to vary with temperature. This is because the rotational and vibrational energies are quantised. There are definite energy levels, just as in the case of the electron energy levels, and energy can only be absorbed in fixed amounts or quanta. As the temperature increases, the energy rises to higher levels and the heat capacity increases. The quanta are much smaller than those of electronic energy, and correspond with wavelengths in the infra-red part of the spectrum. If a beam of infra-red radiation is passed through a molecular substance, the molecules can absorb the wavelengths corresponding to the quanta of rotational and vibrational energy, and thus give what is known as an *infra-red absorption spectrum*.

5.8. Gas density

The ideal gas equation, referring to n moles of gas, is:

$$pV = nRT$$

If the mass of gas is m grams, and its relative molecular mass is M , then

$$n = \frac{m}{M}$$

hence

$$pV = \frac{m}{M} RT$$

$$M = \frac{m RT}{V p}$$

$$= \frac{\rho}{p} RT$$

where ρ is the density of the gas. The units of ρ are g m^{-3} .

This relationship is the basis for several methods of determining the relative molecular mass of a gaseous substance. For some purposes very high accuracy is needed, as for example in the determination of relative atomic masses (§ 2.7); the density measurements can be made with the required accuracy, but since gases do not exactly obey the ideal gas

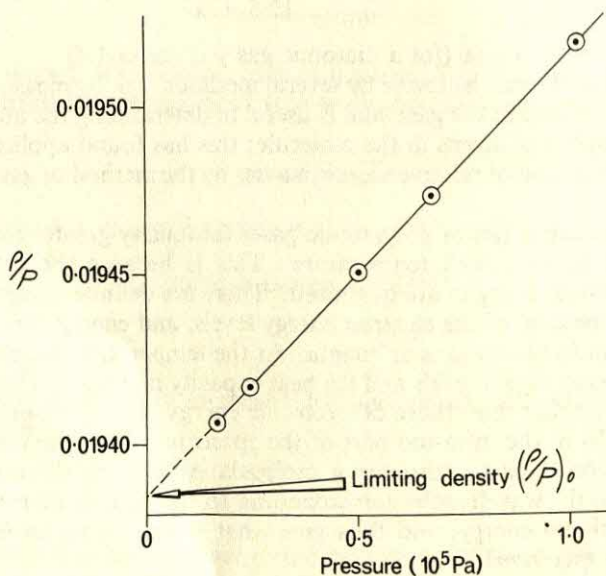


Fig. 25. Graph for obtaining the limiting density of carbon dioxide

equation it is necessary to correct for non-ideal behaviour. We have seen that all gases behave ideally at very low pressures, but it is not possible to measure densities under such conditions, since the mass of a reasonable volume of gas would be too small to measure accurately. However, if the density is measured at several pressures (usually below atmospheric) and the ratio ρ/p is plotted against p , a straight line is obtained (Fig. 25) which can be extrapolated to zero pressure. The value of ρ/p at zero pressure, shown as $(\rho/p)_0$ on the graph, is known as the *limiting density*, and when this is inserted in the equation the accurate value of relative molecular mass will be obtained:

$$M = \left(\frac{\rho}{p} \right)_0 RT$$

Three methods have been used to measure gas densities with high accuracy.

Regnault's method

A glass bulb is evacuated and weighed empty. It is then filled with the gas, the temperature and pressure being recorded, and weighed again: the mass of gas taken is thus found by difference. The volume of the bulb is then determined by filling it with water and weighing again. From the mass of gas and the volume, the density is calculated. Further measurements are now carried out at several different pressures, and the limiting density found by plotting ρ/p against p as already shown. The relative molecular mass may now be calculated.

EXAMPLE

From the graph in Fig. 25, the limiting density of carbon dioxide at 0°C is found to be 0.0193777.

The relative molecular mass is given by:

$$\begin{aligned} M &= \left(\frac{\rho}{p} \right)_0 RT \\ &= 0.0193777 \times 8.3143 \times 273.15 \\ &= 44.007 \end{aligned}$$

(Note that the accurate value of 0°C , in kelvin, is 273.15 K).

To achieve this high degree of accuracy, several corrections are necessary; for example, the small contraction of the bulb when it is evacuated must be taken into account, since this alters the buoyancy of the bulb and therefore its weight in air.

The volumeter method

In this method the gas is produced from a suitable generating apparatus, which is weighed before and after the experiment to obtain the mass of gas. The gas is passed into an evacuated vessel of

accurately known volume, and the pressure is measured. This method differs from Regnault's only in the method of determining the mass, which is simpler and eliminates some of the corrections otherwise required.

The microbalance method

A gas density microbalance (Fig. 26) consists essentially of a beam carrying a closed bulb at one end and a counterpoise weight at the other: the whole assembly is usually made of silica, supported by two thin silica fibres sealed to the centre of the beam. The balance is contained in a glass case, which is connected to a manometer and to apparatus for evacuating the case and admitting gases.

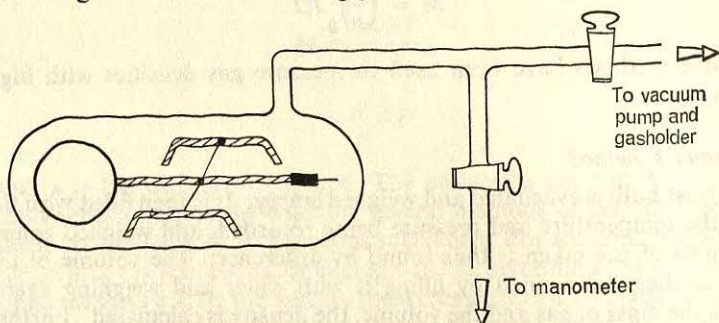


Fig. 26. Gas density microbalance

When there is gas in the case, the upward thrust on the bulb due to its buoyancy causes that end of the beam to rise, and the position of balance depends on the density of the gas. Since the latter is proportional to the pressure, the balance can be set, by adjusting the pressure, so that the pointer at the end of the beam is opposite a fixed mark. This pressure is then recorded. After evacuation, a second gas (e.g. oxygen) of known relative molecular mass is admitted and the pressure adjusted until the pointer rests at the same position as before. The densities of the two gases, at the two recorded pressures, are then equal. The temperature is kept constant during the experiment by immersing the apparatus in a thermostat bath.

Applying the gas equation, for gas (1)

$$M_1 = \frac{\rho_1}{p_1} RT$$

$$\text{and for gas (2) } M_2 = \frac{\rho_2}{p_2} RT$$

but $\rho_1 = \rho_2$, so that

$$\frac{M_1}{M_2} = \frac{p_2}{p_1}$$

Since the two pressures have been measured, and the relative molecular mass of one gas is known, the relative molecular mass of the other gas can be found. To obtain an accurate result, the measurement is repeated at different pressures and then the values of p_2/p_1 are plotted against p and extrapolated to zero pressure to give the limiting value.

5.9. Vapour density measurements

Another application of gas density measurements lies in the determination of relative molecular masses of liquids. The liquid, which should preferably have a low boiling point, is vaporised and the density of the vapour is measured. The methods used are both simpler and quicker than those described in the last section, but are not of high accuracy.

The relative molecular mass is calculated from the measured quantities—*i.e.* the mass of vapour and its volume—from the equation

$$M = \frac{m}{V} \frac{RT}{p}$$

derived above. This means that the vapour is assumed to be an ideal gas; although this is far from true, the low accuracy of the methods used does not justify applying a correction.

An alternative procedure is to calculate the *vapour density*, which is a term that has a special meaning, being defined as the ratio of the mass of a certain volume of vapour to the mass of an equal volume of hydrogen, measured at the same temperature and pressure. From Avogadro's law, the vapour density is therefore equal to the ratio of the mass of a certain number of molecules of the vapour to the mass of the same number of molecules of hydrogen. Hence:

$$\text{Vapour density} = \frac{\text{Relative molecular mass of vapour}}{\text{Relative molecular mass of hydrogen}}$$

and as the relative molecular mass of hydrogen is 2.02:

$$\text{Relative molecular mass of vapour} = 2.02 \times \text{Vapour density}$$

The concept of vapour density, first introduced by Cannizzaro, has now been superseded by the use of the gas equation.

Victor Meyer's method

In this method a known mass of liquid is vaporised and caused to displace air from the apparatus; the volume of the latter is then measured. The apparatus (Fig. 27) consists of a long glass tube ending in a bulb, with a side-arm near the top connected to a gas burette filled with water. The tube is heated to a temperature at least 20 degrees higher than the boiling point of the liquid under investigation, by boiling water (or some other liquid) in the outer jacket. The air in the tube

expands when heated, causing the level of water in the burette to fall: when the level is stationary, the apparatus has attained a steady temperature. The burette is then filled to the top with water.

About 0.1 g of the liquid is put into a small glass bottle, the exact mass being found by weighing the bottle before and after filling.

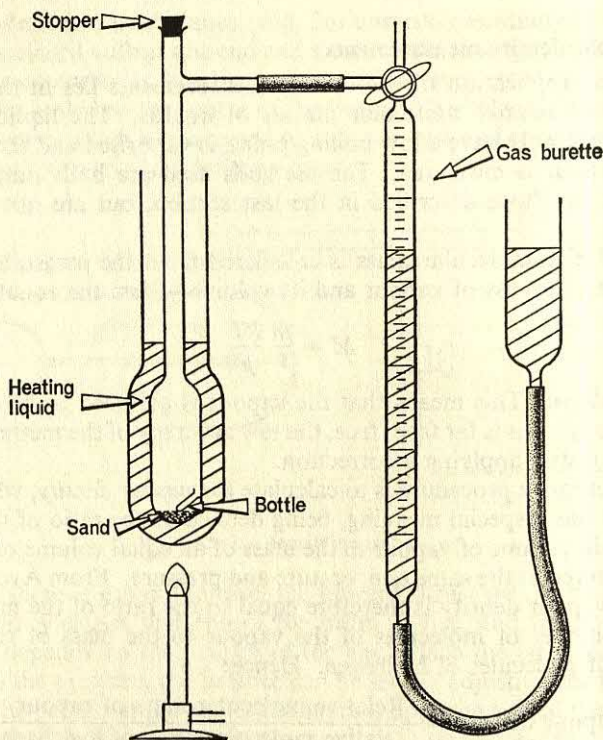


Fig. 27. Victor Meyer's method for measuring the density of vapours

The stopper is removed, the bottle dropped into the tube, and the stopper quickly replaced (there are some variations in the way in which the bottle is introduced, depending on the design of the apparatus). The bottle falls to the bottom of the tube (a little sand breaks its fall) and the liquid vaporises, blowing out its stopper. The vapour displaces its own volume of air into the burette, where the pressure is adjusted to atmospheric by means of the levelling tube, and the volume is then read. The temperature is read on a thermometer placed near the burette, and the barometric pressure is measured. The small displacement caused by replacing the stopper can be found by carrying out a blank experiment without the bottle, and this volume is subtracted to obtain the corrected volume.

Since the air was collected over water, it will contain water vapour, and the law of partial pressures must be applied (*see* p. 60). If the barometric pressure was p_1 Pa, and the temperature was $t^\circ\text{C}$, at which temperature the vapour pressure of water is p_2 Pa, then:

$$\text{Partial pressure of air} = (p_1 - p_2)$$

If the corrected volume of (air + water vapour) was V m³, and the mass of liquid taken was m g, the relative molecular mass is calculated as follows:

$$\begin{aligned} M &= \frac{m RT}{V p} \\ &= \frac{m \cdot 8.31(t + 273)}{V(p_1 - p_2)} \end{aligned}$$

Dumas' method

This method is the same, in principle, as that of Regnault, the vapour being weighed in a bulb of known volume. The glass bulb has a capacity of 100–250 cm³, and the neck is drawn out to a narrow constriction (Fig. 28). The bulb is first weighed, this giving the total mass of the bulb plus the air inside it (m_1). A few cm³ of the liquid under investigation are then introduced by alternately warming the bulb and cooling it with the outlet immersed in the liquid.

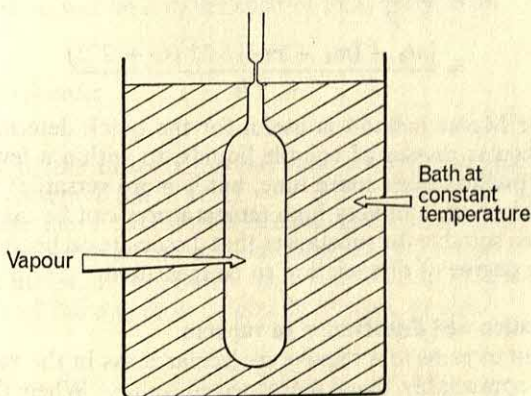


Fig. 28. The vapour density method of Dumas

The bulb is now immersed as far as possible in a bath of water (or oil) and is heated to a temperature at least 20 degrees above the boiling point of the liquid. The temperature of the bath is kept constant until the liquid has completely vaporised, during which the air and excess of vapour are expelled, and the outlet is then sealed with a flame. When

water is used in the bath, the temperature can conveniently be kept constant by keeping the water boiling: the boiling point can be calculated from the barometric pressure (see § 6.5).

The bulb is now allowed to cool, dried and weighed; this gives the mass (m_2) of the bulb plus the amount of vapour required to fill it at the temperature of the bath ($t_1^\circ\text{C}$) and atmospheric pressure (p Pa). The volume of the bulb is found by breaking the tip under water that has previously been boiled to remove dissolved air, when the bulb should fill almost completely with water: a final weighing gives the mass (m_3) of the bulb plus water. Taking the density of water as 10^6 g m^{-3} , the volume of the bulb is given by

$$V = \frac{m_3 - m_1}{10^6} \text{ m}^3$$

To find the weight of the empty bulb, the weight of air in it when it was first weighed must be calculated. The density of air at STP is 1290 g m^{-3} , and the air occupied a volume of $V \text{ m}^3$ at room temperature ($t_2^\circ\text{C}$) and barometric pressure (p Pa), hence the mass of air (m_4) was:

$$m_4 = 1290 V \frac{273}{t_2 + 273} \frac{p}{101\,300}$$

The relative molecular mass can now be calculated in the usual way:

$$\begin{aligned} M &= \frac{m RT}{V p} \\ &= \frac{[m_2 - (m_1 - m_4)] 8.31 (t_1 + 273)}{V p} \end{aligned}$$

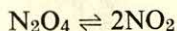
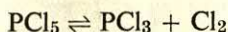
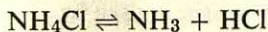
The Victor Meyer method is useful for the quick determination of relative molecular masses of volatile liquids, to within a few per cent. The Dumas method takes more time, but is more versatile: with bulbs made of silica or iridium very high temperatures can be used, and the method is also suitable for substances that dissociate on heating (§ 5.10), enabling the degree of dissociation to be measured.

5.10. Association and dissociation in vapours

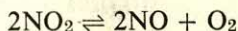
Many substances have a relative molecular mass in the vapour state that differs appreciably from the expected value. When the relative molecular mass is greater than normal, *association* has taken place, so that the observed relative molecular mass is the average value for the single molecules, double molecules, and possibly larger associations, that are present. This phenomenon is usually caused by hydrogen bonds linking the molecules and therefore occurs with substances capable of hydrogen bonding (*e.g.* carboxylic acids and alcohols) as described in § 3.7. Association is less extensive in the vapour than in the liquid state, and decreases as the temperature is raised: thus ethanoic acid ($M = 60$)

has a relative molecular mass of 120 in solution, but only 100 in the vapour state just above the boiling point.

A relative molecular mass value less than the normal indicates that *thermal dissociation* has taken place, i.e. that some of the molecules have been split up into smaller molecules under the action of heat. Typical examples of substances that show this type of dissociation are ammonium salts, halides of non-metals, and dinitrogen tetroxide:



and at higher temperatures:



In such cases it is possible, by measuring the density of the vapour, to determine the extent to which dissociation has occurred: this is expressed as the *degree of dissociation*, defined as *the fraction of the original substance that has dissociated*. Alternatively, the dissociation can be given as a percentage.

To take an actual example, if the degree of dissociation of phosphorus pentachloride is α , then for every mole of PCl_5 originally present α moles will have dissociated, leaving $(1 - \alpha)$ moles undissociated. The products of dissociation will be α moles each of PCl_3 and Cl_2 :



<i>Number of moles</i>	$1 - \alpha$	α	α
------------------------	--------------	----------	----------

The result of the dissociation has thus been to increase the number of moles present from 1 to $(1 - \alpha + 2\alpha) = (1 + \alpha)$. The observed relative molecular mass (M) will be equal to the total mass of the mixture (which is the same as the original mass of PCl_5) divided by the total number of moles. If the relative molecular mass of PCl_5 is M_0 , then this is the mass of the one mole originally present, so that:

$$M = \frac{M_0}{1 + \alpha}$$

This equation only applies to the case where the dissociation of one molecule of a substance produces two molecules of products. This is the most common type of dissociation, but in general if there are N molecules of products then the following equation can be applied to any dissociation reaction:

$$M = \frac{M_0}{1 - \alpha + N\alpha}$$

EXAMPLE

In a Dumas determination, 0.54 g of dinitrogen tetroxide was found to occupy a volume of 201 cm³ at 45°C and 106 kPa. What is the degree of dissociation, assuming that nitrogen dioxide is the only product?



Number of moles $1 - \alpha \quad 2\alpha$

Total number of moles = $1 + \alpha$

The observed molecular weight is given by

$$M = \frac{m RT}{V p}$$

where V is 0.000201 m³ and p is 106 000 Pa

$$M = \frac{0.54 \times 8.31 (45 + 273)}{0.000201 \times 106\,000}$$

$$= 67.0$$

and

$$M = \frac{M_0}{1 + \alpha}$$

where M_0 is the relative molecular mass of N_2O_4 , which is 92.

$$1 + \alpha = \frac{92}{67.0}$$

$$= 1.37$$

$$\alpha = 0.37.$$

The degree of dissociation is 0.37, or the dinitrogen tetroxide is 37% dissociated.

5.11. The Joule-Thomson effect

When a gas is allowed to expand from a high pressure to a lower pressure, there is usually a drop in temperature. This was discovered by Joule and Thomson in 1862, and is known as the *Joule-Thomson effect*. It has been of considerable practical importance in processes for liquefying gases (see § 6.2).

The cooling is due to the fact that when a gas expands the molecules move farther apart, so that work has to be done against the forces of intermolecular attraction. The energy is taken from the kinetic energy of the molecules, so that the temperature of the gas falls. The existence of the Joule-Thomson effect is, in fact, an additional proof that intermolecular forces exist. Some gases (e.g. hydrogen and helium) do not show this effect unless cooled to a low temperature (-80°C in the case of hydrogen): at ordinary temperatures the effect is reversed, and the temperature rises instead of falling. This can be connected with the fact that these gases show no underperfect behaviour at ordinary temperatures (see Fig. 20, the curve for hydrogen at 0°C).

QUESTIONS

G.C.E.

1. (a) How does the pressure of a given mass of gas in a fixed volume change as the temperature is raised? How is this change interpreted in terms of the behaviour of the molecules of the gas?

(b) At 0°C and 1 atm pressure ($1\text{ atm} = 1.013 \times 10^5\text{ Pa}$), a certain mass of gas has a volume of 100.0 cm^3 . The volume of the same mass of the same gas at the same temperature is 2.412 cm^3 at 40 atm, and 1.170 cm^3 at 80 atm pressure. Show that the behaviour of the gas deviates from that of the ideal gas, and explain the reasons for this.

(c) Why does the rate of a reaction such as the decomposition of gaseous hydrogen iodide into hydrogen and iodine vapour increase rapidly with rising temperature? [Oxford]

2. (a) (i) What do you understand by the term *diffusion*? (ii) Two gases can often be separated by diffusion. Explain why this is so, stating any relevant law. Why would it be easier to separate a mixture of argon and helium by diffusion than one of nitrogen and ethane?

(b) 0.254 g of iodine are introduced into an evacuated vessel of volume 100 cm^3 . The vessel is closed and heated to 1473 K . It is found that the pressure of the iodine vapour in the vessel at this temperature is $1.71 \times 10^5\text{ N m}^{-2}$.

(i) Calculate the pressure expected under these conditions if it is assumed that the iodine is wholly in the form of I_2 molecules. (ii) What qualitative inference can be drawn from the difference between your result in (i) and the observed pressure? Make any further deductions you can. [Oxford]

3. Two volumes of hydrogen are mixed with five volumes of dry air at 100°C and atmospheric pressure. The mixture is sparked so that the combustion of hydrogen goes to completion. If air contains oxygen and nitrogen in the molar ratio 1:4, what is the mole fraction of water vapour on the resulting mixture at 100°C ?

A $\frac{2}{3}$ B $\frac{1}{3}$ C $\frac{2}{7}$ D $\frac{1}{4}$ E $\frac{1}{5}$ [Cambridge]

4. Discuss briefly, but critically, the basic postulates underlying the kinetic theory of gases and explain (a) gas pressure, (b) thermal expansion at constant pressure, (c) the use of $\overline{c^2}$, the mean square velocity, in the equation $pV = \frac{1}{3}nmc^2$ where n molecules of ideal gas, each of mass m , occupy a volume V at a pressure p .

Calculate (i) the kinetic energy (in joules) of the molecules in one mole of ideal gas at 47°C ; (ii) the *root* mean square velocity of hydrogen iodide molecules, HI, at 47°C in the gaseous phase (in this calculation the molar mass of hydrogen iodide must be expressed in the appropriate SI unit, *i.e.* the *kilogram*); (iii) the *ratio* of the *root* mean square velocities of oxygen, O_2 , and hydrogen iodide at 47°C ; (iv) the time expected to be taken for a given volume of hydrogen iodide at 47°C to effuse (or diffuse) through a pin-hole if the same volume of oxygen under the same conditions takes 60 seconds. (v) Compare this with that predicted by Graham's Law of Diffusion, which should be stated.

$\text{H} = 1, \text{O} = 16, \text{I} = 127, R = 8.314\text{ J K}^{-1}\text{ mol}^{-1}, 0^\circ\text{C} = 273\text{ K}, \text{J} = \text{kg m}^2\text{ s}^{-2}$.

[S.U.J.B.]

5. What is meant by an ideal gas? Discuss the ways in which the behaviour of real gases deviates from ideality, giving reasons for such deviations. How does the kinetic theory of gases lead to an explanation of: (a) the relative rates of diffusion of gases; (b) the increased rate of reaction at higher temperatures?

Calculate the root mean square velocity of oxygen molecules at 298 K. ($R = 8.3 \text{ J K}^{-1} \text{ mol}^{-1}$) [W.J.E.C.]

6. Discuss the assumptions on which the kinetic theory of ideal gases is based and state the equation which governs the behaviour of such gases.

The van der Waals equation for one mole of a gas,

$$(P + a/V^2)(V - b) = RT \quad (a \text{ and } b \text{ are constants})$$

is often used to describe the behaviour of real gases. Suggest reasons for the terms a/V^2 and b in this equation.

Explain why, under the same conditions, different gases diffuse at different rates. A vessel saturated with aqueous ammonia is placed at one end of a narrow tube 1 m long and one saturated with concentrated hydrochloric acid at the other. Describe and explain what happens. [J.M.B.]

7. (a) Discuss briefly, but critically, the basic postulates underlying the kinetic theory of gases, explaining the development of gas pressure and how, in general terms, the theory leads to Avogadro's Law. Derivations of formulae are not required.

(b) For a given mass of gas (*e.g.* carbon dioxide) over a range of temperature, sketch the graphs which are usually obtained on plotting (i) p (pressure) against V (volume), (ii) pV against p . Account for what is seen and contrast with what would be obtained using an ideal gas.

(c) Without describing experimental procedure, explain briefly how the method of limiting densities enables relative molar masses (molecular weights) of gases and vapours to be determined accurately. Outline how the atomicity of oxygen can be deduced from studying the densities of oxygen and oxygen-bearing gases and vapours measured under the same conditions.

(d) Deduce the molecular formula of ozone from the following observations, given that ozone reacts with unsaturated hydrocarbons of which turpentine is a convenient source.

When ozonised oxygen is shaken with turpentine at room temperature and pressure the contraction in volume is *twice* the expansion in volume obtained on heating an equal volume of the same sample of ozonised oxygen until nothing further happens and cooling to the same initial conditions.

[S.U.J.B.]

CHAPTER 6

LIQUIDS

6.1. The liquefaction of gases

Any gas can be liquefied if cooled to a sufficiently low temperature, that is, to a point where the kinetic energy of the molecules is no longer great enough to overcome the intermolecular forces. On the other hand, many substances which are gaseous at ordinary temperatures may be converted to liquids simply by increasing the pressure (e.g. ammonia, carbon dioxide and sulphur dioxide): the liquid may then be kept stored under pressure, as in the case of liquid sulphur dioxide in the usual glass syphons.

It follows that the necessary conditions for the liquefaction of a gas involve both the temperature and the pressure. Raising the pressure brings the molecules closer together and so increases the influence of the intermolecular forces, but is not sufficient to cause liquefaction unless the temperature is low enough. This is illustrated by the fact that some gases will not liquefy at ordinary temperatures, no matter how high the pressure. At one time (about 1860) it was thought that hydrogen, oxygen and nitrogen could not be liquefied at all, since the lowest temperatures then available and pressures of many thousands of atmospheres had failed to accomplish it.

The exact conditions of temperature and pressure required for liquefaction were first discovered by Andrews in 1869. In his experiments, some carbon dioxide gas was enclosed in a capillary tube maintained at constant temperature, and the volume occupied by the gas was measured at different pressures up to about 10^7 Pa. When the volume readings were plotted against the pressure, a set of curves of the type shown in Fig. 29 were obtained. Each curve corresponds with one particular temperature, and is therefore called an *isotherm* (Greek *isos*, "equal").

At temperatures above 31°C no liquefaction was observed. The 48°C isotherm approximates to the type of curve that is obtained if p is plotted against V in accordance with the Boyle's law relationship $pV = \text{Constant}$, while as the temperature is reduced towards 31°C the isotherms become distorted owing to increasing non-ideal behaviour of the gas. Below 31°C Andrews found that each isotherm consisted of three distinct parts. Starting from point A on the 13°C isotherm, for example, and increasing the pressure, the carbon dioxide remained gaseous until point B. Between B and C the gas liquefied, thus causing a considerable decrease in volume, but the pressure remained constant.

As there was now only liquid in the tube, further increase in pressure caused very little change in volume, so that between C and D the curve was almost vertical. The three sections of the isotherm can be summarised as follows:

AB Gas only present. A normal type of pV curve, allowing for non-ideal behaviour.

BC Gas and liquid present together. The pressure remains constant, while the volume varies with the relative amounts of gas and liquid.

CD Liquid only present. The volume decreases only slightly with increase in pressure, since liquids have a very low compressibility.

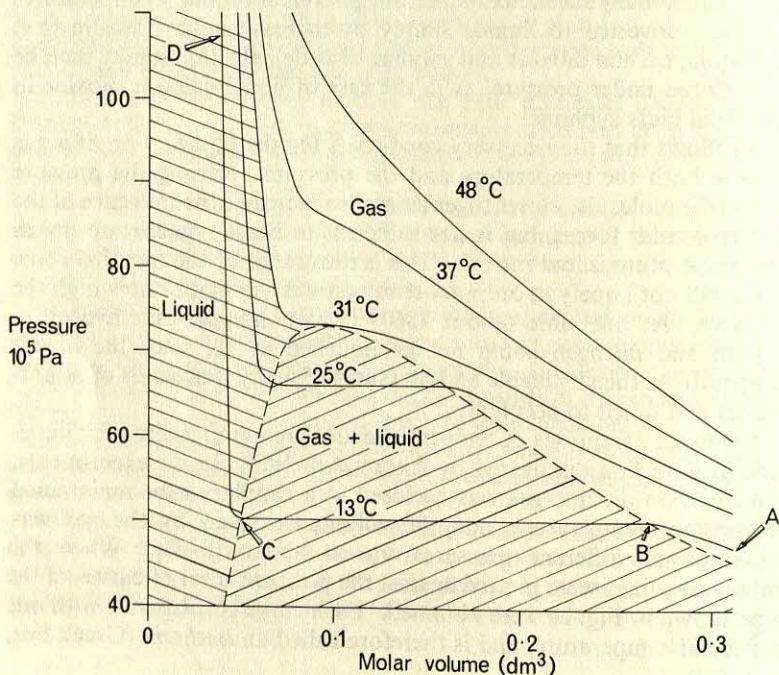


Fig. 29. Pressure-volume isotherms for carbon dioxide

At higher temperatures the horizontal portions of the isotherms decrease in length, until at 31°C there is only a point of inflexion, *i.e.* the isotherm becomes horizontal at a single point. The dotted line encloses the region where both liquid and gas can exist together, while the other areas show where the carbon dioxide is either gaseous, or wholly in the liquid state.

This experiment shows that in order to liquefy the gas, the temperature and pressure must be such that the isotherm passes through the area bounded by the dotted line. The maximum temperature at which this

can happen is the temperature of the isotherm which just touches the peak of the dotted curve (for carbon dioxide, 31°C). This is called the *critical temperature*, which may therefore be defined as *the temperature above which the gas cannot be liquefied, no matter how high the pressure*.

The pressure required to liquefy a gas at the critical temperature is known as the *critical pressure*: for carbon dioxide it is 7400 kPa. If the temperature happens to be below the critical temperature, the gas will liquefy at a somewhat lower pressure.

The conditions for liquefaction of a gas may now be stated:

- (a) The temperature must be at, or below, the critical temperature.
- (b) A suitable pressure must be applied, equal to the critical pressure if the temperature is at the critical temperature, but becoming less if the temperature is reduced below this value.

When a substance is at both the critical temperature and the critical pressure, an interesting situation arises. At this point, which is where the 31°C isotherm in Fig. 29 touches the dotted curve, both gas and liquid would occupy the same volume and therefore their densities are equal: there is, therefore, no difference between liquid and gas at the critical point. This can be demonstrated by heating a tube containing both gas and liquid until the critical temperature is reached (Fig. 30). At that point the liquid, instead of evaporating, reaches the same density as the gas above it, and the meniscus separating the two disappears. This is another method by which the critical constants of a gas may be measured.

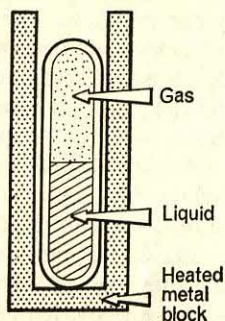


Fig. 30. Determination of critical temperature by the disappearing meniscus method

TABLE 4. CRITICAL CONSTANTS

	Critical temperature (K)	Critical pressure (kPa)
helium	5	230
hydrogen	33	1300
nitrogen	126	3400
oxygen	154	5000
ethene	283	5200
carbon dioxide	304	7400
hydrogen sulphide	374	9000
dichlorodifluoromethane	385	4100
ammonia	406	11 300
chlorine	417	7700
sulphur dioxide	430	7900

A list of critical constants is given in Table 4. It will be noticed that helium, hydrogen, nitrogen and oxygen all have very low critical temperatures, so that a considerable degree of cooling is necessary before they can be liquefied. Gases that have critical temperatures above normal room temperature (carbon dioxide and the gases below it in the table) can be liquefied by compression and stored under pressure in the liquid form.

6.2. Methods of liquefaction

There are many important applications of gas liquefaction, including the attainment of low temperatures, the separation of gases by liquefaction followed by distillation, and the advantages of storing and handling substances in the liquid state rather than as a gas.

Moderately low temperatures are obtained by using the refrigerator principle. Here the working substance is a gas with a critical temperature well above ordinary room temperature, so that it can be liquefied by compression. The liquid is then allowed to evaporate, causing heat to be extracted from the container which is being cooled. Refrigerators use gases such as ammonia, sulphur dioxide or dichlorodifluoromethane, and the practical lower limit to the temperature that can be reached is about -40°C . A lower temperature (-80°C) can be reached with solid carbon dioxide ("dry ice"), which is produced by allowing liquid carbon dioxide to evaporate quickly. Much lower temperatures can be reached with liquid oxygen (boiling point -183°C), liquid nitrogen (-195°C), liquid hydrogen (-253°C) and liquid helium (-269°C), and they are used for many purposes both in research and in industry when very low temperatures are required.

The liquefaction of air is an industrial process of great importance, because the oxygen and nitrogen (which have different boiling points) can be separated by fractional distillation (*see* § 10.2). This method has the additional advantage that the oxygen is produced in the liquid form and can be transported in insulated lorries to the distributing centre before being evaporated and compressed into the familiar cylinders. Another example of the transport of liquefied gas on a large scale is the shipment of natural gas (methane) as a liquid in insulated ships: the boiling point is -162°C .

Many of the gases mentioned above have very low critical temperatures, so that before they can be liquefied they must be cooled well below normal temperatures. The critical temperatures of air, hydrogen and helium, for example, are all below -100°C . Such temperatures cannot be reached by normal methods of cooling, *i.e.* freezing mixtures or refrigerators. There are, however, two other methods of cooling which may be used.

The Joule-Thomson effect (§ 5.11) can be used to cool any gas that is below the inversion temperature; this applies to both oxygen and nitrogen at ordinary temperatures, so air can be liquefied by this means.

liquid air is continuously fractionated as it is formed, oxygen (which has the higher boiling point) being left as a liquid while the nitrogen escapes from the column as a gas.

6.3. The liquid state

The molecules in a liquid have a lower kinetic energy than they would have in the gaseous state, but they are still moving at high velocity, as can be seen from the fact that most liquids flow readily. Liquids also have the ability to diffuse, as can be shown by carefully pouring two miscible liquids into the same container, with the heavier liquid at the bottom: the boundary between the liquids will, in the course of time, disappear. However, owing to the very small distances between the molecules in a liquid, the independent motion of molecules is greatly hindered and both the fluidity and the rate of diffusion is very much less than in the case of a gas.

The close proximity of the molecules also results in the properties of liquids being greatly influenced by the intermolecular forces. The most obvious example of this is the fact that a liquid has a definite surface, which a gas has not. The existence of a surface means that molecules which are at the surface are normally unable to break away. Fig. 32

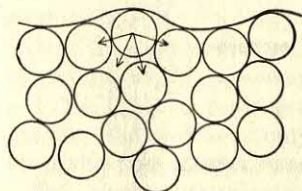


Fig. 32. Inward pull on molecules at the surface of a liquid, owing to intermolecular attraction

shows how a molecule at the surface is subject to forces of intermolecular attraction, which produce a resultant force tending to prevent the molecule leaving the surface. Since this force is acting simultaneously on all the molecules at the surface, the whole of the surface of a liquid is subject to an inward pull: this force is called the *surface tension*. If a small drop of one liquid is suspended in another liquid (e.g. a drop of oil in water), the drop will always

tend to assume a spherical shape since the force of surface tension causes the surface to contract to the smallest possible size. A drop of water on a greasy surface behaves in a similar way, but is not quite spherical because the weight of the drop tends to flatten it out. Surface tension is also responsible for liquids "bumping" when boiled (see § 6.5).

6.4. Vapour pressure

The intermolecular forces in a liquid prevent most molecules from escaping from the surface. Owing to the exchange of energy in molecular collisions, however, some molecules will have a kinetic energy much above the average value: the energy distribution will be similar to that of molecules in a gas (see Fig. 18). If a molecule at the surface has sufficient energy to break loose from the forces that are tending to hold it back, it can escape from the liquid; this causes *evaporation* of molecules

into the gaseous state. Any liquid will therefore have above its surface a certain amount of material in the form of vapour.

If the liquid is put into a closed vessel, the space above it being evacuated (Fig. 33), molecules of vapour will fill the space and the concentration of vapour molecules will steadily increase as evaporation takes place. The rate of evaporation will depend on the proportion of molecules with sufficient energy to escape, which in turn depends on the temperature of the liquid, so that if the temperature is kept constant the rate of evaporation will also be constant. Some of the vapour molecules, which will be moving in all directions, will strike the surface of the liquid and will be held there by the intermolecular forces, so that *condensation* will also be taking place all the time. The rate at which molecules of vapour strike the surface is proportional to the concentration of molecules in the vapour. As evaporation proceeds, the number of molecules in the vapour increases, so that the rate of condensation also increases; when it reaches the same value as the rate of evaporation, no further change will take place in the concentration of vapour molecules. When a balance is reached between two opposing processes, *equilibrium* has been established. In that case, the liquid and vapour are in equilibrium because the rate of condensation is equal to the rate of evaporation.

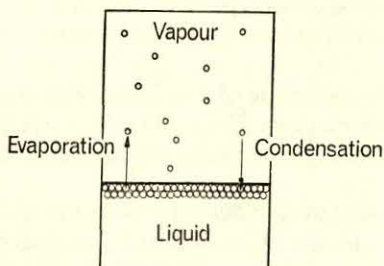


Fig. 33. Vapour-liquid equilibrium

The pressure exerted by the vapour is known as the *vapour pressure* and, since it depends on the concentration of molecules in the vapour, the vapour pressure of a liquid will be a constant value for any definite temperature. If the temperature is raised, the kinetic energy of the molecules is greater and a higher proportion will escape from the surface. A new equilibrium will be reached, with a higher vapour pressure: the vapour pressure thus increases with rise in temperature. The relationship is not a linear one, and a typical vapour pressure curve is shown in Fig. 34.

The pressure exerted by the vapour is known as the *vapour pressure* and, since it depends on the concentration of molecules in the vapour, the vapour pressure of a liquid will be a constant value for any definite temperature. If the temperature is raised, the kinetic energy of the molecules is greater and a higher proportion will escape from the surface. A new equilibrium will be reached, with a higher vapour pressure: the vapour pressure thus increases with rise in temperature. The relationship is not a linear one, and a typical vapour pressure curve is shown in Fig. 34.

6.5. The boiling point

If a liquid is heated in an open vessel, a point will be reached where the vapour pressure is equal to the atmospheric pressure (*see* Fig. 34). Bubbles of vapour can now form inside the liquid, and being lighter than the liquid they rise to the surface and break—in fact the liquid boils. The boiling point is thus a constant for any particular external pressure: what is called the normal boiling point refers to a pressure of 101.3 kPa, and for accurate work a correction must be applied depending

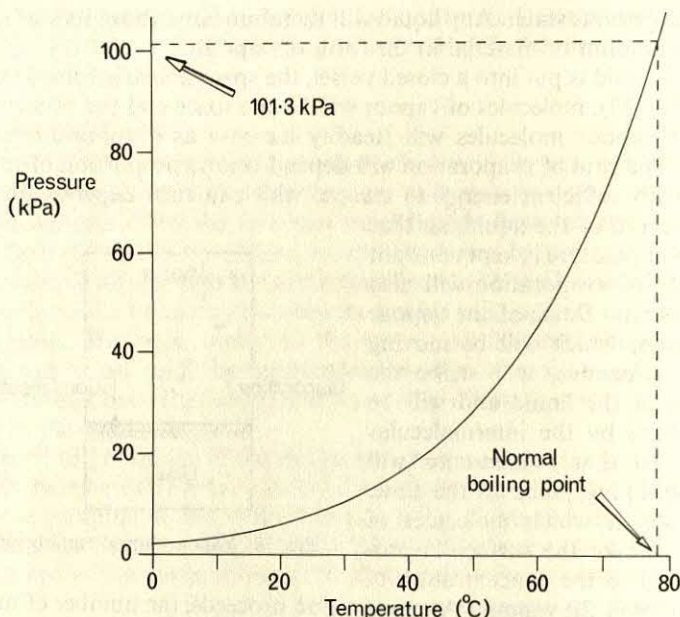


Fig. 34. Vapour pressure curve for ethanol

on the actual barometric pressure. Changes in atmospheric pressure are not very large, and the variation may be taken as approximately linear. Thus the boiling point of water at atmospheric pressure changes by 0.28 K for a change in pressure of 1 kPa, *e.g.* at 103.3 kPa it is 100.56°C. If the pressure is reduced (as in distillation under reduced pressure) the boiling point is much lower than at atmospheric pressure, and so liquids which decompose at their normal boiling point can be safely distilled in this way.

It is frequently found that when a liquid is heated to cause it to boil, boiling starts with a sudden and perhaps violent evolution of bubbles, commonly described as *bumping*. If a thermometer is placed in the liquid just before boiling starts, it will be found that the temperature is much above the true boiling point. A liquid in this state is said to be *superheated*. The phenomenon is particularly noticeable when the vessel is smooth and the liquid is dust-free, and it is caused by the surface tension of the liquid. In the absence of surface tension forces, a bubble of vapour that has formed in a liquid would have a pressure of vapour inside it only slightly greater than the external pressure on the liquid (owing to the small pressure caused by the weight of liquid above it). The surface tension, however, will tend to contract the surface of the bubble, so that an additional pressure is required to balance this. It can be shown that this excess pressure becomes larger as the size of the

bubble is reduced, so that the formation of a small bubble requires a vapour pressure much above the external pressure on the liquid, and therefore a temperature well above the normal boiling point. Once the bubble is formed, however, it will grow very rapidly, since the pressure required becomes less as the size increases; this causes sudden evolution of large quantities of vapour. Superheating can be considerably reduced by providing rough surfaces on which bubbles of vapour can form more easily, *i.e.*, with a lower internal pressure. Small pieces of broken unglazed tile are commonly used for this purpose, or alternatively several capillary tubes sealed at one end, with the open ends immersed in the liquid.

The boiling point of a *pure* liquid is a useful aid to identification, particularly in the case of organic compounds. When measuring boiling points, care must be taken to see that superheating of the liquid is either avoided or reduced to a minimum.

The effect of superheating may be overcome by placing the thermometer in the vapour from a boiling liquid instead of in the liquid itself (Fig. 35 (a)). Vapour condenses on the cold thermometer bulb, thus warming it up, and the temperature recorded by the thermometer will rise steadily to a maximum value. At this point, the film of liquid on the bulb is in equilibrium with the vapour, so that the temperature is the true boiling point at the prevailing atmospheric pressure. If plenty of liquid is available, and particularly if the vapour is inflammable or

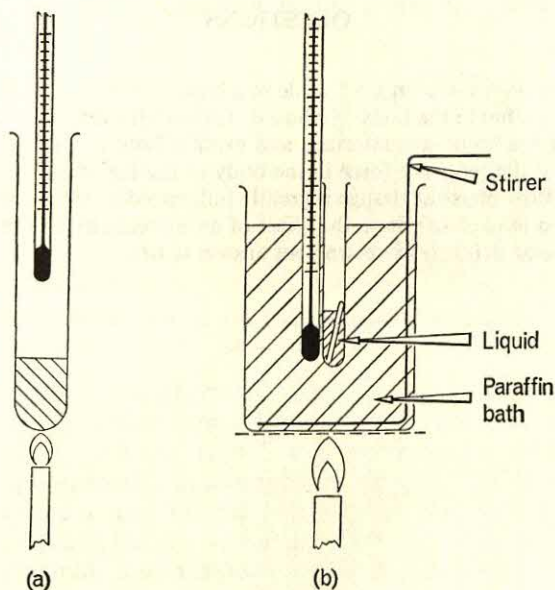


Fig. 35. Determination of the boiling point of a liquid
(a) Thermometer bulb in the vapour (b) Siwoloboff method

harmful, it is better to use a distillation apparatus (*see* Fig. 72) for this type of measurement.

When only a small quantity of liquid can be used, and an accuracy of about 0.5 K is sufficient, the Siwoloboff method is useful (Fig. 35 (b)). The liquid is contained in a small test-tube attached to a thermometer, which is heated in a liquid paraffin bath. A capillary tube sealed at one end is dropped, open end downwards, into the liquid. On heating the bath, air will bubble slowly out of the end of the capillary tube as the temperature rises and the air expands. When the boiling point is reached, bubbles of vapour can form readily at the end of the capillary tube with very little superheating, and there will be a continuous stream of vapour bubbles. The temperature at which this occurs may be taken as the boiling point, or the bath may be allowed to cool down until the evolution of bubbles *just* stops; the latter gives a slightly more accurate figure.

It has already been pointed out (§ 4.2) that boiling points increase (a) with increasing molecular size, (b) with increasing polarity of the molecule, and (c) when molecular association occurs. It follows that in groups of compounds with the same type of molecular structure (*e.g.* a homologous series of organic compounds) the boiling-point will increase regularly with increasing relative molecular mass (*see* Table 3).

QUESTIONS

G.C.E.

1. The resultant force on a molecule in a liquid is different at the liquid-gas interface from that in the body of a liquid. (a) Give the direction of this resultant force at the liquid-gas interface and explain how it arises. (b) Give the magnitude of the resultant force in the body of the liquid and explain how it arises. (c) What physical change is greatly influenced by the magnitude of the phenomenon in (a)? (d) State the effect of an increase in temperature on the physical change in (c). (e) Explain your answer to (d). [J.M.B.]

CHAPTER 7

SOLIDS

7.1. The structure of solids

A solid has many characteristic properties that distinguish it from a liquid or a gas. The most important are regularity of form and rigidity. The molecules (or ions) in a solid do not have sufficient kinetic energy to move about at random, so that they are held at fixed positions by the attractive forces. The only form of molecular motion that takes place is vibration about these fixed positions; rotation of the molecules hardly ever occurs in solids. The resulting structure is therefore close-packed and rigid, so that solids are usually hard and do not tend to alter their shape or volume to any great extent under varying conditions of temperature and pressure. In addition, many solids have a regular geometrical form: such a solid is referred to as a *crystal*. If the individual crystals of a pure solid substance are examined, it is found that they all have the same angles between the various faces, though the actual shape may vary with the conditions under which they were formed (Fig. 36). This regularity of the crystalline form results from a regular, geometrical arrangement of the molecules from which the crystal is made up.

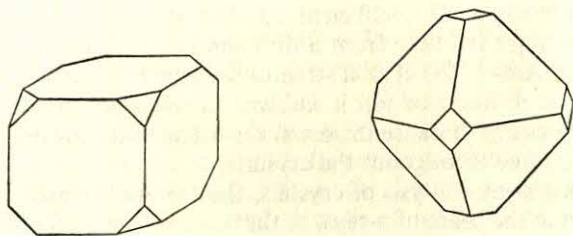


Fig. 36. Possible different forms of a sodium chloride crystal grown under different conditions

Some materials, although showing many of the properties of a solid, do not possess crystalline form. These are called *amorphous* (from the Greek *a-morphe*, "without form") and include glass, rubber, many plastics, red phosphorus and amorphous sulphur. They do not behave entirely like pure solids: for example, they do not melt sharply at a definite temperature, but tend to soften on heating and gradually change into a viscous liquid. Such materials are usually regarded as *supercooled liquids*, and not as solids in the strict sense of the word. There are also other solid substances which, although not crystalline in form, show

some degree of regular structure. Fibres, both natural (silk, wool, etc.) and man-made (e.g. nylon), and stretched rubber show this characteristic. It is generally considered, however, that the true solid state of a pure substance is always crystalline.

7.2. Crystal structure

The regular external form of crystals suggests that the molecules or ions of which they are composed must also be arranged in a regular manner. A plane containing atoms all at equal distances apart would act as a diffraction grating* to radiation of suitable wavelength—in this case about 10^{-10} m, since the sizes of atoms are of this order and the atoms in a solid are closely packed. This wavelength lies in the x-ray region, and on this reasoning Laue suggested that x-rays might be diffracted by crystals. He proved this to be the case by passing a beam of x-rays through a crystal of zinc blende on to a photographic plate: a definite diffraction pattern was obtained, consisting of a central dark spot (caused by part of the beam passing undeviated through the crystal) surrounded by a number of smaller spots arranged in a regular pattern.

It was later shown by Sir William Bragg and his son that when a beam of monochromatic x-rays (i.e. rays all of the same wavelength) was reflected by the face of a crystal, only a few definite angles of incidence gave bright reflected beams: this is identical with the behaviour of a beam of monochromatic light reflected from a diffraction grating. They were further able to prove, from measurements of these angles, that the distances between the planes of atoms in the crystal could be calculated. If a sufficient number of such measurements are made, reflecting each time from a different set of atom planes, the internal dimensions of the crystal structure can be built up until the exact position of each atom or ion is known. It must be remembered that this is only possible because the distances between the atoms in any one plane is the same throughout the crystal.

In modern x-ray analysis of crystals, the material is finely powdered and rotated in the beam of x-rays, so that a complete picture is obtained in a short time. This is the *powder camera* method of Debye, Scherrer and Hull. Beams of electrons or neutrons are also sometimes used in place of x-rays to obtain additional information about the positions of the atoms.

7.3. Crystal lattices

When the dimensions of the crystal structure have been determined, a model of the crystal may be made showing the position of the various

* A *diffraction grating* usually consists of a number of parallel lines ruled on a plate. If light of wavelength similar to the distances between the lines is passed through the plate, or reflected from it, interference occurs and a diffraction pattern of alternate light and dark bands results.

units of structure (which may be molecules, atoms or ions). This pattern is known as the *crystal lattice* (or *space lattice*) and gives only the positions, not the actual sizes, of the units. Since exactly the same pattern is repeated throughout the crystal, it is only necessary to include sufficient of the lattice to show the basic pattern. Some of the simpler types of crystal lattice will now be described.

Elements

In solid elements, the units of structure are atoms and they are held together either by valence forces (chemical bonds) or by the van der Waals forces (§ 4.2). Fig. 37 shows the two ways in which carbon

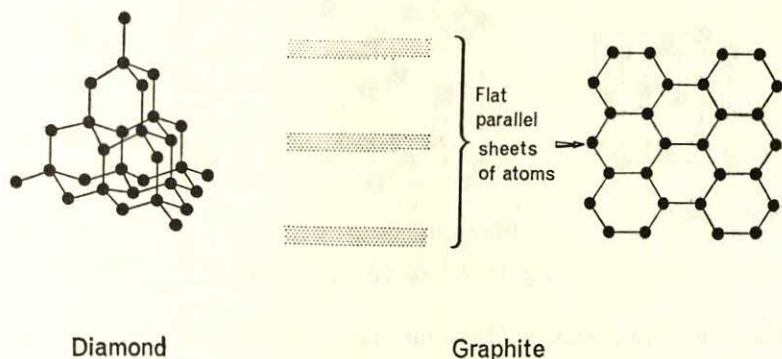


Fig. 37. Crystal structure of the allotropic forms of carbon

crystallises, *i.e.* as diamond or graphite. In the diamond crystal each carbon atom is surrounded by four other atoms at the tetrahedral angles of the normal carbon valences, and the C—C distance is 154 pm, corresponding closely to the distance between two carbon atoms joined by a single bond in an organic compound. It is evident that each carbon atom throughout the crystal is joined to four other carbon atoms by covalent bonds, so that the whole crystal is a three-dimensional *giant molecule*. Diamond is therefore very hard and rigid, but brittle since the structure cannot be distorted to any great extent without breaking the bonds. Graphite shows a very different type of structure, with the carbon atoms arranged in flat sheets separated by quite a large distance (341 pm). The hexagonal arrangement of the atoms in the layers is almost exactly the same as in benzene and condensed-ring aromatic hydrocarbons, and the interatomic distance of 142 pm is only slightly greater than in such compounds. The distance between the layers, on the other hand, is much greater than could be accounted for by a chemical bond: the forces holding the layers together must therefore be of the van der Waals type. This type of structure is called a *layer lattice*, and the lubricating properties of graphite arise from the ability of the layers of atoms to slip over

one another, since the forces between the layers are relatively weak and non-directional. Other elements from the same group of the periodic table also have crystal lattices similar to diamond, while members of the other non-metallic groups (VB, VIB, VIIB) have structures which depend, as with carbon, on the number and direction of their valence bonds.

The metallic elements have simple crystal lattices, and nearly all of them crystallise in one of three forms (Fig. 38), of which the face-centred cubic and the close-packed hexagonal represent the closest possible way in which a collection of spherical objects can be packed.

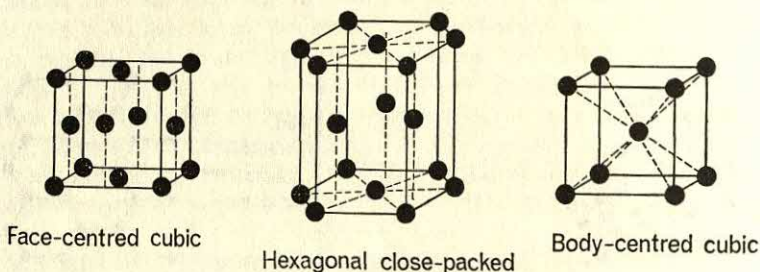


Fig. 38. Crystal lattices of metals

The term "close-packed" does not only mean that the atoms are close together, but that the maximum number are packed into a given volume; to illustrate this, if some marbles (all of equal size) are packed in a box, layer by layer, so that they take up the minimum of space, they will be found to take up one of the two arrangements mentioned above. This type of arrangement is consistent with the theory of the metallic bond (§ 3.6), since the atoms are so close together that there must be chemical bonding, while the way in which the atoms are packed shows that the bonds are non-directional. The close-packing makes most metals hard, but at the same time they are ductile and can be made to flow if subjected to a high enough pressure. This is another result of the non-directional nature of the bonds.

Compounds

Turning from elements to compounds, those with covalent bonding will first be considered. They include the majority of organic compounds (except the salts of organic acids and bases), and those inorganic compounds which are not predominantly electrovalent. The molecule is now the unit of structure, with van der Waals forces holding the molecules together. The molecules will be arranged regularly at the lattice points, and will orientate themselves to give the best packing, as shown in the carbon dioxide crystal (Fig. 39). It will be seen that the individual atoms of carbon and oxygen are also arranged in regular

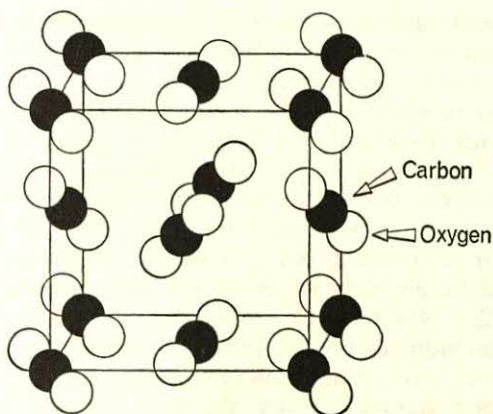


Fig. 39. A molecular lattice: the crystal structure of carbon dioxide

order, so that x-ray investigation will show the exact position of all the atoms. In this way the bond lengths and bond angles can be determined by measurements on crystals, and so the structure of the molecules can be arrived at. This is the most important application of crystal structure measurements. One of the most recent successes in this field has been

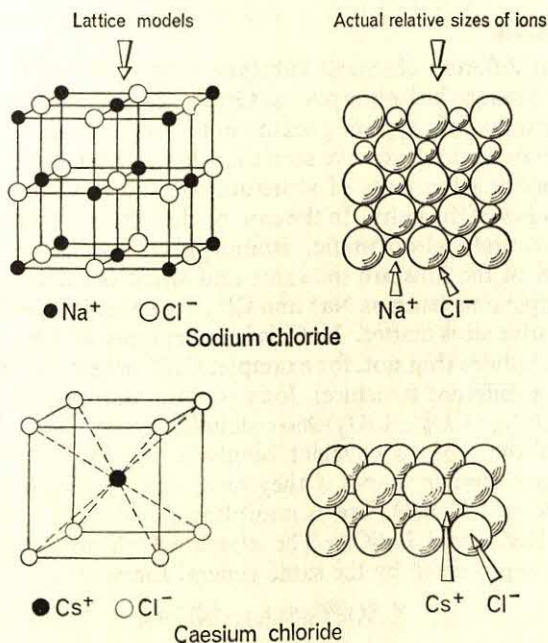


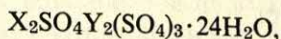
Fig. 40. Ionic crystals, showing both the crystal lattice and the actual packing of the ions

the elucidation of the structure of DNA (deoxyribonucleic acid), the extremely complex molecule that has been shown to be the carrier of genetic information in human cells.

As examples of electrovalent compounds, the chlorides of sodium and caesium will be considered (Fig. 40). These both crystallise in cubic lattices, that of sodium chloride being face-centred cubic (*i.e.* having one ion at the centre of each face of the cube) and that of caesium chloride body-centred cubic (where there is an ion at the centre of each cube). If either of these lattices is examined, it will be seen that no one ion is attached to any other particular ion—in other words no “molecules” of NaCl or CsCl can be picked out. This shows that the units of structure are individual ions. The forces holding them together are the electrostatic forces of attraction between oppositely charged ions, which are non-directional, so that the ions can pack together in the most efficient way; the type of lattice which results depends on the relative sizes of the two types of ion present. In the case of sodium chloride, the sodium ion is smaller than the chloride ion (the radii are in the ratio 0.52:1) and only six chloride ions can be packed around one sodium ion. The caesium ion, however, is larger and almost the same size as a chloride ion (ionic radii ratio 0.93), so that the packing is eight chloride ions around every caesium ion, resulting in the body-centred cubic lattice.

7.4. Isomorphism

When two different chemical substances have the same crystalline form they are said to be isomorphous (Greek *iso-morphe*, “equal form”). For this to happen, the type of packing in the crystal lattice must be the same in both cases, and we have seen that this depends on the nature of the forces holding the units of structure together and on the relative sizes and shapes of the units. In the case of electrovalent salts, where the forces are entirely electrostatic, isomorphism can occur when the relative sizes of the ions are the same and when the ions have similar shapes. Simple ions (such as Na^+ and Cl^-) are spherical, so in their case only the relative sizes matter. NaCl is isomorphous with KCl and many other alkali halides (but not, for example, CsCl, where the relative ionic sizes cause a different structure). Ions containing more than one atom (*e.g.* SO_4^{2-} , NO_3^- , CO_3^{2-} , ClO_3^-) have definite shapes depending on the direction of the various covalent bonds in the ion. Such ions will normally have similar shapes if they have similar chemical formulae: thus K_2SO_4 and K_2SeO_4 are isomorphous, and so are NaNO_3 and CaCO_3 , KMnO_4 and BaSO_4 . The *alums*, which are all double salts that can be represented by the same general formula,



are all isomorphous; X is a monovalent ion (usually K, Na, or NH_4) while Y is a trivalent metal such as Al, Fe or Cr.

If a solution made by dissolving two isomorphous salts is evaporated until solid begins to crystallise out, the crystals that form are found to contain both salts, in the same proportion as in the original solution. The crystals are homogeneous (*i.e.* they have the same composition throughout), and are referred to as *mixed crystals* or *solid solutions*. This is clearly seen if one of the salts is coloured (*e.g.* K_2SO_4 and K_2CrO_4), when the crystals will be uniformly coloured but the intensity will depend on the proportion of chromate in the mixture.

Another property of isomorphous materials is that they can form *overgrowths*. If a crystal is suspended in a saturated solution of another substance with which it is isomorphous, the crystal will grow with no alteration in shape, since the deposit of the second substance will have the same structure as the original crystal.

7.5. Heat capacities of solids

The molecules (or ions) in a solid cannot move about and normally cannot rotate; they can, however, vibrate about their mean positions. The kinetic energy in solids is therefore entirely vibrational energy. When energy is supplied in the form of heat, the units vibrate faster and the temperature rises. It was discovered in 1819, by Dulong and Petit, that the heat capacities of solid elements, measured at ordinary temperatures, had an almost constant value of $26 \text{ J K}^{-1} \text{ mol}^{-1}$.

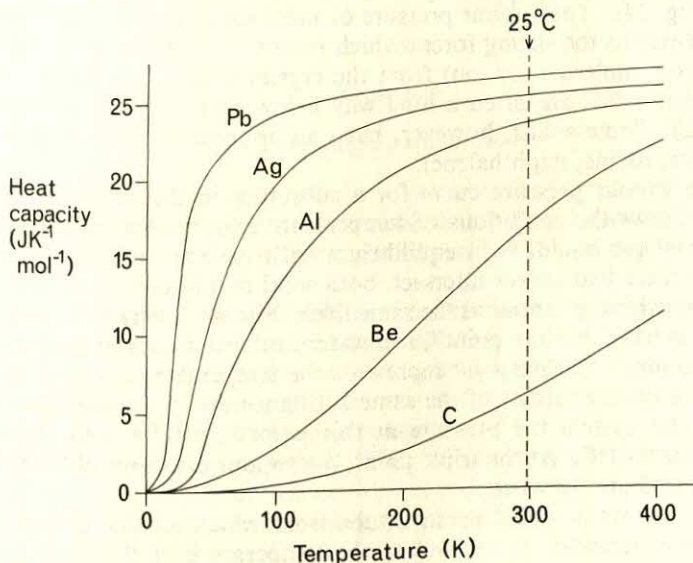


Fig. 41. Heat capacities of elements

In terms of the specific heat capacity, this rule may be expressed as:

$$\text{Atomic mass} \times \text{Specific heat capacity} = 26 \text{ J K}^{-1} \text{ mol}^{-1}$$

approximately.

Dulong and Petit's law was valuable at one time in finding the approximate relative atomic mass of elements, for the purpose of fixing relative atomic masses (§ 2.7). There are, however, exceptions to the rule: certain elements (*e.g.* carbon, beryllium, boron) have heat capacities which are a good deal less than $26 \text{ J K}^{-1} \text{ mol}^{-1}$. The reason for this may be seen by reference to Fig. 41, which shows that the heat capacity varies with temperature, but may reach a maximum value of about $26 \text{ J K}^{-1} \text{ mol}^{-1}$ at a certain temperature (called the *characteristic temperature* of that element). It so happens that the characteristic temperature of most elements is below room temperature, but in the case of carbon and a few other elements it is much higher. Such elements will naturally be exceptions to the rule if the specific heat capacity is measured at room temperature. It has already been explained (§ 5.7) why heat capacities involving vibrational energy increase with temperature, in the light of the quantum theory.

7.6. The vapour pressure and melting points of solids

Solids have a vapour pressure, and this arises in exactly the same way as in the case of a liquid (§ 6.4). Consequently, at any particular temperature the vapour pressure has a definite value, which increases with rise in temperature, following a curve similar to that for a liquid (*see* Fig. 34). The vapour pressure of most solids is very small: this is due partly to the strong forces which have to be overcome in order to remove a molecule (or ion) from the crystal lattice, and partly to the fact that solids are often a long way below their melting points (*e.g.* metals). Some solids, however, have an appreciable vapour pressure (*e.g.* ice, iodine, naphthalene).

The vapour pressure curve for a substance in the solid (or liquid) form shows the conditions of temperature and pressure under which the solid (or liquid) is in equilibrium with the vapour. At the point where these two curves intersect, both solid and liquid can be in equilibrium with the vapour at the same time. Fig. 42 illustrates this: at the point marked "Triple point", ice, water and water vapour can exist in equilibrium. A *triple point* represents the temperature and pressure at which any three states of the same substance are in equilibrium. For the water system the pressure at this point is 610 Pa, and the temperature 0.01°C . At the triple point, the vapour pressures of both solid and liquid are the same.

If some ice is sealed up in a tube from which all the air has been removed, it will start to melt at the temperature of the triple point, and the pressure in the tube will then be 610 Pa. As long as all three phases (ice, water and water vapour) are present, the temperature and

pressure will not alter. Ice therefore melts at 0.01°C at a pressure of 610 Pa, but if the pressure is increased the melting point is lowered, as shown by the third line in the diagram, which shows the temperature at which ice and water can be in equilibrium at different pressures: the system is now not in equilibrium with water vapour. The melting point is usually defined as *the temperature at which both solid and liquid states of a substance are in equilibrium at a pressure of 101 kPa*. For water this is at 0°C .

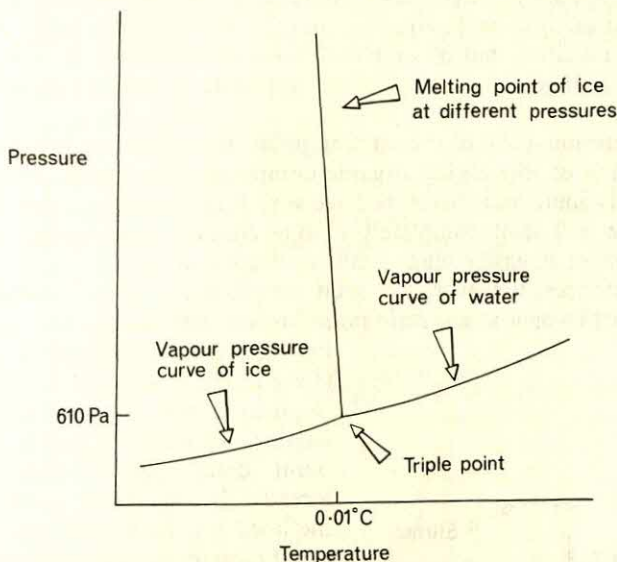


Fig. 42. The triple point of water

Since the triple point for water is easier to reproduce accurately than the melting point of ice, it has replaced the latter as a thermometric standard (see Appendix I).

When a solid has a greater volume than the corresponding liquid (as with water, where an expansion occurs on freezing), the melting point decreases with increasing pressure. Normally, however, the transition from liquid to solid involves a decrease in volume; in that case the melting point increases with increasing pressure, and the melting point line in Fig. 42 would slope to the right. This behaviour can be predicted by the application of a useful rule known as *Le Chatelier's principle*, which states that *if a change occurs in one of the conditions (e.g. temperature or pressure) under which a system is in equilibrium, the system will tend to adjust itself so as to oppose the effects of that change*. Thus if the system consists of ice and water in equilibrium at a particular pressure, and the

pressure is then increased, the system will tend to alter so as to reduce the pressure. This can be achieved by the melting of some of the ice (resulting in a reduction of the volume), and the latent heat thus absorbed would lower the temperature. The new equilibrium would therefore be at a higher pressure and a lower temperature. If, on the other hand, there is a decrease in volume when the liquid freezes, then at a higher pressure some of the liquid would tend to freeze and the latent heat liberated would raise the temperature: in this case the melting point would increase with increasing pressure.

Le Chatelier's principle has a fundamental thermodynamic basis and applies to all systems in equilibrium (chemical as well as physical). It is only qualitative, but of wide usefulness in predicting the direction in which a change will occur. Other applications will be seen in later chapters.

The determination of the melting point of a substance is of great use as a means of identifying organic compounds (inorganic compounds are mostly ionic and therefore have very high melting points). A pure substance will melt completely at one definite temperature, and the measurement is easily made with reasonable accuracy. A mixture of two substances, however, will melt over a range of temperatures, *i.e.* it will start to melt at a certain point but will not become entirely liquid

until a higher temperature is reached (*see* § 8.10). It is essential, therefore, to purify a material (*e.g.* by recrystallisation) before carrying out a melting point determination if it is not already in the pure state. Two methods are in general use for the rapid measurement of melting points.

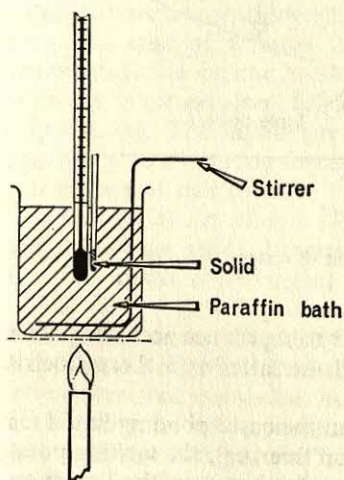


Fig. 43. Determination of melting point: capillary tube method

The capillary tube method

The material, in powder form, is packed into the bottom of a thin-walled capillary tube, which is then attached to a thermometer so that the powder is on the same level as the bulb. The thermometer and tube are heated in a bath of liquid paraffin (Fig. 43) which is kept well stirred, and the temperature at which the solid begins to melt is noted. In order

to reduce superheating, the rate of heating near the melting point should not exceed about one degree per minute: it is best to find the approximate melting point first, then allow the bath to cool a few degrees and perform the accurate measurement with a fresh sample. The accuracy obtained is about ± 0.5 K.

The block method

In this method a small amount of the substance is placed on the polished top of an aluminium block, which is heated directly by a bunsen flame (Fig. 44). Better temperature uniformity is obtained if the sides of the block are lagged with asbestos cord. The temperature of the block is measured on a thermometer inserted in a hole in the block, good thermal contact being obtained by nearly filling the hole with a liquid of high boiling point (*e.g.* liquid paraffin). The substance is covered with a small watchglass to minimise convection cooling due to air currents. After a first rough determination, an accurate figure is obtained by heating a fresh sample slowly over the last few degrees

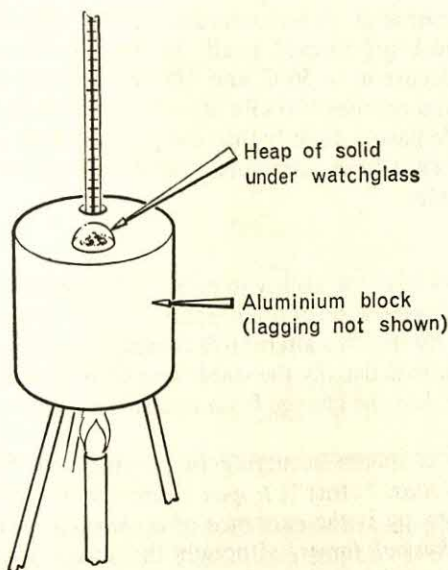


Fig. 44. Determination of melting point: block method

until the first signs of melting are observed. Melting points determined in this way may be 1–2 K lower than those given in tables, since most of the latter will have been measured by the capillary method. The block method gives a slightly lower level of accuracy than the capillary tube method, but less time is required for a determination. The block method is unsuitable for substances which readily sublime (*see below*), or which are rapidly oxidised when heated in air.

7.7. Sublimation

When a vapour is cooled, under certain conditions it will condense directly to a solid. This will happen when the pressure of the vapour is less than the vapour pressure of the solid at the melting point. Thus if

the partial pressure of water vapour in the atmosphere is less than 610 Pa (which is the vapour pressure of ice at 0°C), then cooling will result in the direct formation of ice; this is the way in which frost is formed on a cold night. Conversely, solids which have high vapour pressures will evaporate at a measurable rate, the solid being transformed directly into vapour. This process is termed *sublimation*. Since the vapour can be condensed again to solid on a cold surface, sublimation can be used as a means of purification. Another important application of sublimation is the removal of water from substances which would be damaged by heating (e.g. penicillin), by the process of *freeze-drying*. In this method the wet material (or solution) is frozen, and the water vapour is pumped off under low pressure.

Some solids sublime at all temperatures, under normal atmospheric pressure, no liquid being formed at all. In the case of carbon dioxide, the triple point occurs at -56°C and 500 kPa pressure. The vapour pressure of the solid reaches 100 kPa at -78°C and at this temperature the carbon dioxide passes directly into the gaseous form: liquid carbon dioxide can only exist under pressure. Hence the name "dry ice" for solid carbon dioxide.

7.8. Allotropy

Most substances have the ability to crystallise in more than one form: this is termed *polymorphism* (Greek *polus*, "many"; *morphe*, "form") and is illustrated by the two alternative forms of carbon (diamond and graphite). One form is usually the stable one at any particular temperature and pressure, but the change from one structure to another may be very slow.

In the case of elements occurring in polymorphic forms, the term *allotropy* (Greek *allos*, "other"; *tropos*, "manner") is used. The usual definition of allotropy is *the existence of a chemical element in two or more different physical forms*, although the term is sometimes also applied to compounds, and to forms that are chemically different (e.g. oxygen and ozone). The two main types of allotropy are *enantiotropy* and *monotropy*.

Enantiotropy

In this case each allotrope is stable over a particular range of temperatures and pressures. These ranges do not overlap, so that only one form is stable under any given set of conditions. Solid sulphur, for example, can exist in either the monoclinic or the rhombic form. The pressure-temperature diagram (see Fig. 45) shows how each form is stable within a particular region of the diagram. At atmospheric pressure, rhombic sulphur is the stable form up to a temperature of 95.6°C (point A) but at this point it changes to monoclinic. Above this *transition temperature* the monoclinic form is stable up to the melting point at 119°C (point B). The transition temperature increases with pressure

because the transition from rhombic to monoclinic is accompanied by an increase in volume: this is shown by the line AD.

At the transition temperature, a slight increase or decrease in the temperature will cause rhombic to change to monoclinic and vice versa. The change is therefore a reversible one, and this is a characteristic of enantiotropic behaviour.

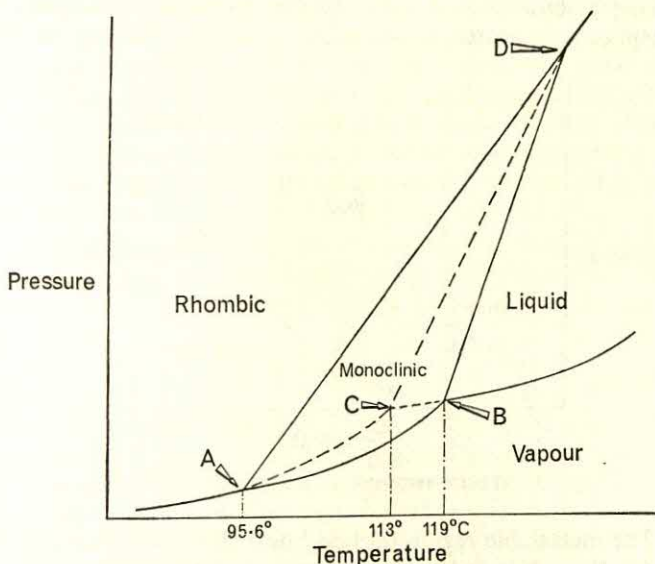


Fig. 45. Pressure-temperature diagram for sulphur

It must not be thought that such changes will take place rapidly: they are, in fact, extremely slow. If rhombic sulphur is heated quickly, it will pass the transition point and reach its own melting point of 113°C , there being no time for the change into monoclinic to take place. The dotted lines in the diagram show the vapour pressure curves for rhombic and liquid sulphur in this region. These curves represent *metastable* equilibrium, so called because although these conditions can be realised in practice the system will eventually revert to the stable form (*i.e.* monoclinic). The point C therefore represents a metastable triple point.

The melting point of monoclinic sulphur varies with pressure along the line BD. The point D occurs at a very high pressure (greater than 10^8 Pa) and the diagram has been distorted in order to show this. Above the point D, monoclinic sulphur cannot exist at all.

Monotropy

If there is only one stable allotrope (the other being metastable), the term "monotropy" is used. Carbon is an example of this type of

allotropy, graphite being the stable form and diamond the metastable. All diamonds are therefore changing into graphite, though fortunately this takes place so slowly as to be unnoticeable.

Another example is phosphorus, with the white metastable form and the stable red form (it is actually violet in the pure crystalline state). The diagram for phosphorus (Fig. 46) shows the vapour pressure curves of red phosphorus and liquid phosphorus as the only stable equilibria, giving a triple point far above atmospheric pressure. This means that if red phosphorus is heated it will sublime before reaching the melting

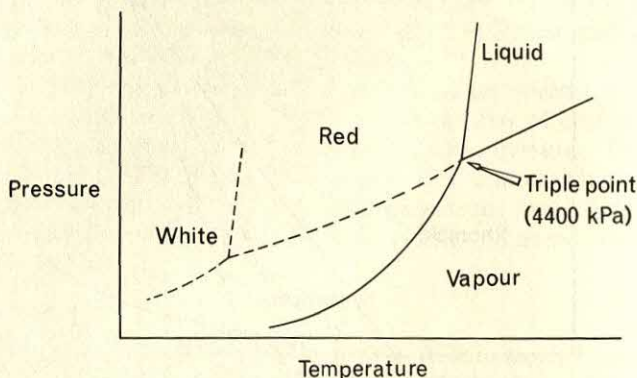


Fig. 46. Pressure-temperature diagram for phosphorus

point. The metastable region (dotted lines) shows the vapour pressure curves for the white form and for supercooled liquid: this gives a metastable triple point. The vapour pressure curves of the two solid forms do not meet, so that there is no way in which one may change reversibly into the other. The white form will change slowly into the red, because the latter is the only stable form under all conditions, but the reverse process (red direct to white) cannot occur. White phosphorus can be prepared from red by an indirect method, however, via the vapour. Heating red phosphorus produces vapour by sublimation: if the vapour is then brought into contact with a cold surface, so that it is suddenly cooled, it condenses to the metastable white form.

7.9. The phase rule

In this (and the preceding) chapter there have been many examples of the different types of equilibrium that can occur between the various possible states of a substance, *e.g.* solid/liquid, liquid/vapour, one allotropic solid form with another, etc. One feature of such equilibrium systems is that each state of the substance is separated from the rest of the system by a definite boundary. In a mixture of ice, water and water vapour, for example, the ice and water have surfaces which separate them from each other and from the vapour. The different

parts of a system separated in this way are called *phases*, so that in the example just given there are three phases, *i.e.* ice (solid phase), water (liquid phase) and vapour (gas phase). Each phase is *homogeneous* (meaning of *constant composition throughout*), so that a phase can be defined as *a homogeneous part of a system separated from other parts of the system by definite bounding surfaces*. When two or more phases are present the whole system obviously cannot have the same composition throughout, and systems containing more than one phase are said to be *heterogeneous*.

The pressure-temperature diagrams which have been used in previous sections (Figs. 42, 45 and 46) show the conditions under which the various possible phases of a substance can exist together. These diagrams are therefore *phase diagrams*. When there is only one solid phase, the solid-liquid-vapour diagram takes the form shown in Fig. 47. The

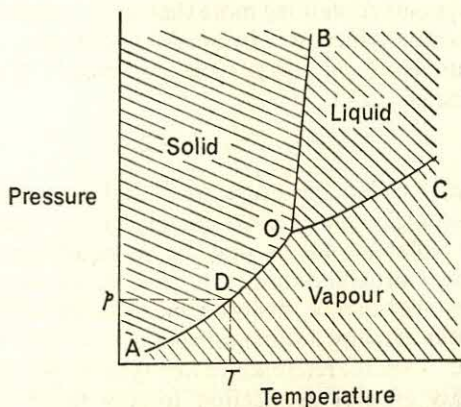


Fig. 47. One-component phase diagram

shaded areas show the conditions of temperature and pressure under which the substance can exist in one particular phase. Within these areas both the temperature and the pressure can be altered independently, provided one of the boundary lines is not crossed, without causing a change of phase. We can put this more shortly by saying that there are two *degrees of freedom*. The number of degrees of freedom of a system is *the number of variables that must be fixed in order to define the state of the system completely*. In this case the only variables are the temperature and pressure; in systems containing more than one substance there will be a third variable, the composition.

The lines separating the phase areas in Fig. 47 represent the conditions under which any two phases can be in equilibrium; OA for solid/vapour, OB for solid/liquid, OC for liquid/vapour. When two phases are present it is only possible to alter one of the variables; for

example, if the temperature of a solid/vapour system is fixed at T (point D on line OA), then the pressure must be p if equilibrium is to be maintained. There is thus only one degree of freedom. The point O shows all three phases in equilibrium, and at this point both the temperature and the pressure are fixed, so that there are no degrees of freedom.

If the number of phases (P) in equilibrium is compared with the number of degrees of freedom (F) it will be seen that there is a simple relationship between the two:

Number of phases (P)	1	2	3
Number of degrees of freedom (F)	2	1	0
$P + F$	3	3	3

We can therefore write $P + F = 3$ for a system containing a single substance in various possible phases, *i.e.* a *one-component* system. It is found that for systems containing more than one component the number of degrees of freedom is increased by one for each additional component, so that if the number of components is represented by C the relationship can be put in the general form:

$$P + F = C + 2$$

This expression is called the *phase rule*. It is extremely useful as a means of predicting, for a particular system, (a) the number of possible ways in which different phases may be in equilibrium, and (b) the number of degrees of freedom in each case. It has been shown above how the phase rule can be deduced empirically from actual phase diagrams, but it is actually a fundamental law and can be derived from thermodynamics, without reference to any type of phase diagram at all. It is of perfectly general application to any heterogeneous system, whether physical or chemical, and its only limitation is that it predicts *all possible equilibria*; this will include conditions of metastable equilibrium, which it may not always be possible to observe in practice.

As an example of the use of the phase rule, consider the case of sulphur. Pure sulphur is a single chemical substance (one component, *i.e.* $C = 1$), but it can exist in four different states: solid (rhombic), solid (monoclinic), liquid and vapour. Each of these states constitutes a separate phase, because there is always a surface separating one from another, as between liquid and vapour, solid and liquid, rhombic crystals from monoclinic crystals. For a one-component system the phase rule becomes

$$F = 3 - P$$

and since the number of degrees of freedom (F) cannot be less than zero it follows that it is impossible for all four of the possible phases to be in equilibrium at the same time. A glance at the sulphur diagram (Fig. 45) confirms this. If there are three phases in equilibrium ($P = 3$),

there will be no degrees of freedom, and this can therefore happen at certain fixed points on the diagram. There are four possible combinations of four phases taken three at a time, so there should be four such points on the diagram (points A, B, C and D; note that C represents metastable conditions). The correct number of two-phase equilibria can be predicted in the same way and these will have one degree of freedom so that they appear on the diagram as lines separating the two phases.

Phosphorus has the same number of possible phases as sulphur, so the phase rule would give exactly the same predictions. In this case, however, some equilibria that the phase rule shows to be *possible* cannot be observed experimentally.

Examples of the application of the phase rule to two-component systems will be given in later chapters.

QUESTIONS

G.C.E.

1. The properties of substances are largely the result of the type and strength of bonding between the particles of which they are composed.

Critically discuss this statement and in your answer refer specifically to the following substances: silica, graphite, sodium chloride, iodine and metallic copper.

[London]

2. Give a definition of "melting-point". Explain, from the viewpoint of the kinetic theory, what changes take place when the temperature of a solid is raised to the melting-point. Describe concisely how you would measure the melting-point of a solid, of which only a few milligrams were available. Explain carefully the difference between what takes place during the melting of pure and impure specimens of a substance, and show how the melting-point may be used as a criterion of the purity and for the identification of substances.

[J.M.B.]

3. State and explain what happens when (a) rhombic sulphur is heated to 100°C ; (b) white phosphorus is heated in nitrogen to 200°C ; (c) a little red phosphorus is heated strongly in a narrow glass tube, sealed at one end; (d) liquid mercuric iodide is cooled to room temperature.

What is the arrangement of the carbon atoms in graphite and in diamond?

[Oxford]

CHAPTER 8

SOLUTIONS

8.1. The nature of solutions

A solution is a homogeneous mixture of two or more different substances. This means that the molecules of the two components (solvent and solute) are distributed uniformly throughout the whole of the solution. Another way of putting it is to say that a solution is a one-phase system, since the solution, being a molecular mixture, has no surfaces separating any one part from another. If, however, the solution is in equilibrium with a second phase (*e.g.* excess of solid, or a gas), then the system would be heterogeneous.

The extent to which one material (solute) will dissolve in another (solvent) is governed by the following factors:

(a) The attractive forces between the solute and solvent molecules, compared with the attractions that the solute (or solvent) molecules have for each other.

(b) Solvation of the solute, *i.e.* the attachment of molecules of the solvent to solute molecules or ions, either by electrical attraction or chemical bonding.

The effect of unlike intermolecular forces can be approached by considering whether, say, pentane (a liquid hydrocarbon, with non-polar molecules and therefore small attractive forces) will mix with water, where the molecules are polar and the intermolecular forces are also increased by the formation of hydrogen bonds. It will be difficult, in the first place, for pentane molecules to force their way between the strongly attracted water molecules; it will also be difficult for the water molecules to pass into the pentane, since they cannot easily break away from the adjacent water molecules. Very little mixing will take place—in other words, neither liquid is more than very slightly soluble in the other. This is an extreme case of differing intermolecular forces, and where there is less difference the mutual solubility will correspondingly increase. To take the other extreme, if two liquids have almost identical attractive forces there will be nothing to stop the molecules of the liquids from mixing completely.

It is more difficult for a solid to dissolve in a liquid than for one liquid to dissolve in (*i.e.* mix with) another liquid. This is due to the much stronger forces holding the molecules together in the solid, which have to be overcome before the molecules can pass into the liquid phase and mix with the molecules of solvent. High solubility therefore requires

strong attractive forces between solvent and solute molecules. The strongest forces of this kind are those between ions and polar solvent molecules, where the electrical attraction is so strong that the ions, when in solution, will have molecules of solvent attached to them: this is known as *solvation*. Since electrical forces are inversely proportional to the square of the distance, a small ion will be more solvated than a large one because the solvent molecules can approach closer to the charge. The water molecule is highly polar and so water is an excellent solvent for ionic substances, the solvation which takes place in this case being referred to as *hydration*. Fig. 48 shows how the ions of sodium chloride hydrate in solution; the number of water molecules attached to an ion is not a fixed quantity, but the illustration shows the average number.

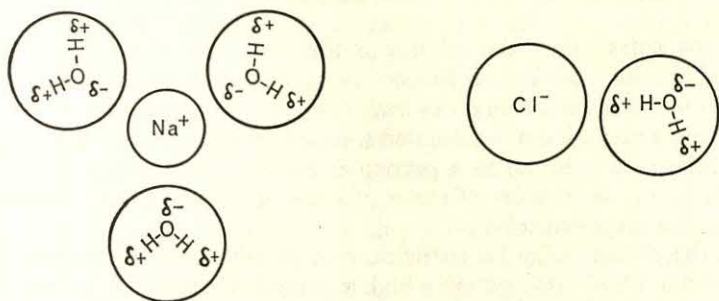


Fig. 48. Hydration of ions

If both solvent and solute consist of polar molecules there is also strong electrical attraction, in this case between the two dipoles. This is likely to give good solubility, and solvation can again occur. Solvation of molecules is often increased by the formation of hydrogen bonds.

It follows that polar solvents (and particularly water) are good solvents for polar molecules and for ionic substances, whereas non-polar solvents will dissolve non-polar molecules but will be poor solvents for polar molecules or ions. This may be expressed shortly as "like dissolves like."

8.2. The solubility of solids in liquids

When a solid is shaken up with a liquid at a constant temperature, after a time a point is reached when no more solid will dissolve. The solution is then said to be *saturated*. We have here an example of a state of equilibrium, where the rate at which solid is dissolving is equal to the rate at which material crystallises out again from the solution. The equilibrium is not affected by the amount of solid present, since if a

small area of surface is considered, the rate at which molecules escape from the surface depends on the number of molecules in that area of surface, which remains constant, so that

$$\text{Rate of dissolution} = \text{Constant}$$

while the rate at which molecules return to this portion of the surface of the solid is proportional to the concentration of those molecules in the solution (c), hence,

$$\text{Rate of recrystallisation} = \text{Constant} \times c$$

At equilibrium,

$$\begin{aligned}\text{Rate of dissolution} &= \text{Rate of crystallisation} \\ c &= \text{Constant}\end{aligned}$$

The concentration of the solution is therefore constant as long as an excess of solid is present. It follows that *a saturated solution is a solution that is in equilibrium with an excess of solid at a given temperature.*

The concentration of a saturated solution represents what is called the *solubility* of a material in a particular solvent. It is expressed as the *molality*, i.e. the number of moles of solute dissolved in 1 kg of solvent to form a saturated solution.

In the absence of solid particles, it is possible for a solution to be *supersaturated*, i.e. to contain a higher concentration of the solute than does a saturated solution. Such solutions may be prepared by making a solution that is nearly saturated (but entirely free from solid) at a certain temperature, and then cooling it. Since the solubilities of most substances decrease as the temperature is reduced, the solution will now be supersaturated, but it is unlikely that solid will form at once, since it is difficult for crystals to start growing unless there is a solid nucleus on which the growth can start. If a small crystal of the solute is added, solid will at once crystallise out and equilibrium will be established. This is known as "seeding" the solution. The presence of dust particles, or small particles of glass caused by scratching the walls of the container with a glass rod, will have the same result in relieving supersaturation.

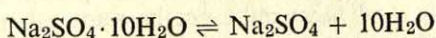
Very small particles of solid have a greater solubility than the normal value, a fact first discovered by Ostwald. This has some importance in gravimetric analysis, because precipitates, when first formed, frequently contain extremely small particles which can pass through a filter paper (e.g. the precipitate of barium sulphate, in the determination of sulphate). If the precipitate is allowed to stand for a time before filtering, preferably hot, the smallest particles will slowly redissolve, the solid being redeposited on the larger particles. The process is sometimes called *granulation* of the precipitate. Gravimetric measurements involving the precipitation of so-called "insoluble" compounds are actually based on

the fact that these substances are only sparingly soluble, so that the amount of material remaining in solution is negligibly small. The same principle is used in qualitative analysis when metals are precipitated as sparingly soluble chlorides, sulphides, sulphates and hydroxides.

In accordance with the general principles expressed above, water is a good solvent for ionic compounds (inorganic and organic salts), and for organic molecular solids which are strongly polar and particularly those with which the water molecules can form hydrogen bonds, *i.e.* molecules containing the groups —O—H (alcohols, aldehydes, carbohydrates, phenols, carboxylic acids) and >N—H (amines, amides). The solution will consist of a homogeneous mixture of water molecules and hydrated solute molecules or ions. Many inorganic salts, however, have a very low solubility, as shown by the examples of sparingly soluble substances given above. Ethanol acts as a solvent for the same classes of compounds, but the solubility of salts is lower than in water.

For organic solvents in general, solubility is likely to be high when solute and solvent have molecules of similar size and polarity, or both contain hydrogen-bonding groups. Non-polar solvents (*e.g.* benzene, tetrachloromethane) and weakly polar ones (*e.g.* ethoxyethane) do not dissolve salts at all, a fact which is often put to practical use when it is desired to extract an organic material from an aqueous solution containing salts (*see* § 8.6).

Solubilities generally increase with rise in temperature, often very considerably. Applying Le Chatelier's principle, as the temperature is raised the system will tend to oppose the change, *i.e.* to absorb heat. Since the result is that more material dissolves, it follows that the process of solution is usually accompanied by an absorption of heat. This is due to the energy required to pull the molecules or ions away from the crystal lattice (known as the *lattice energy*). Where solvation occurs, however, energy is also *liberated* during the process. The result of this can be seen by comparing the effect of temperature on the solubilities of various inorganic salts in water (Fig. 49), when it will be seen that the solubilities of certain salts vary very little with temperature (in some cases, *e.g.* calcium citrate, the solubility may even decrease as the temperature is raised). This is because the energy of hydration almost balances the lattice energy, so that the overall energy change is nearly zero; this may occur in the case of anhydrous salts, *e.g.* NaCl. On the other hand, when salts are hydrated already in the solid state (*e.g.* $\text{Na}_2\text{SO}_4 \cdot 10\text{H}_2\text{O}$) the energy of hydration is bound to be small and the solubility increases with rise in temperature. Sodium sulphate is a very good example of this behaviour, because at 32°C the hydrate changes to the anhydrous form, and the solubility of the latter actually decreases with temperature. The solubility curve therefore has a break at 32°C , which is the transition temperature for the equilibrium:



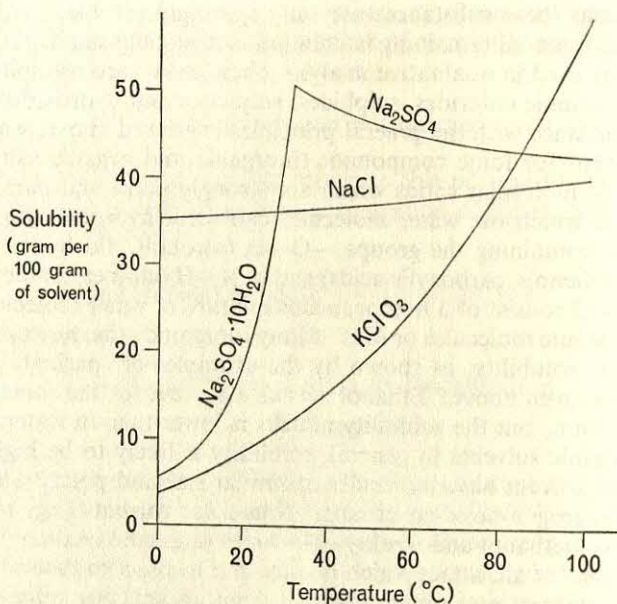


Fig. 49. Solubility curves for some inorganic salts in water

8.3. Determination of solubilities of solids

The first step is to prepare a saturated solution. Some of the solid is finely powdered (so that it may dissolve more rapidly) and is put with the solvent into a stoppered vessel, which is kept at constant temperature and shaken frequently. If all the solid dissolves, more must be added, so that an excess is always present and equilibrium between solid and solution can become established. There is only one certain way of finding out when the solution is saturated, and that is to analyse the solution at intervals until the concentration shows no further change.

The analysis involves removing a measured quantity of the solution and determining the amount of solid that it contains. If the temperature is not too high, the sample may be removed with a pipette, the mass of the sample being calculated from the volume and the density. If the solubility curve is steep, and the solution is much above room temperature, some solid will crystallise out as the solution cools, so that a pipette cannot be used. At the higher temperatures, therefore, some of the solution is sucked into a weighed vessel, which is then reweighed to find the mass of the sample. The solution and any solid that has crystallised out can then be washed out and analysed.

Saturated solutions may contain fine solid particles, which do not settle out quickly, and these must not be removed with samples for analysis or the result would give too high a figure for the solubility.

The solution must therefore be filtered, one method being to fit the sampling pipette with a rubber tube packed with cotton wool.

The weight of solid present in the sample may be found in one of the following ways:

(a) *By evaporating the solution* to dryness and weighing the solid that is left. This is best carried out on a water bath. It takes a long time, and is not suitable for solids that either decompose or evaporate at this temperature.

(b) *Chemical analysis.* This is more accurate, and if there is a suitable volumetric method it is much quicker. Acids, for example, can be titrated with standard alkali, bases and salts of weak acids with an acid, oxidisable substances with manganate(VII), halides with silver nitrate, etc.

8.4. Separation by crystallisation

If a solid is dissolved in the minimum quantity of hot solvent and the solution is then cooled, most of the solid will usually crystallise out. This is because solubilities usually decrease as the temperature is lowered. The solubility curve for potassium chlorate(V) in Fig. 49 shows that 100 g of water at 100°C will dissolve 56 g of KClO_3 . The solubility at 20°C is only 5 g, so that if the solution is cooled to this temperature the excess (51 g) will crystallise out. If the solid is now filtered off, a further quantity can be crystallised by boiling the solution in order to evaporate some of the water (the 5 g of solid left in solution will only require $100 \times 5/56 = 9$ g of water to keep it in solution at 100°C) and again cooling (the solid retained in solution will now be $5 \times 9/100 = 0.45$ g, so that 4.5 g will have crystallised).

If the original solid happens to be impure, the impurity will be retained in solution during the crystallisation if its solubility at the lower temperature is greater than the amount actually present. It is therefore possible to purify solids by recrystallisation providing that:

(a) A solvent is chosen such that the solubility of the solid is low at room temperature and high when the solvent is hot. If this condition is not satisfied, it will be impossible to obtain a reasonable yield of recrystallised material.

(b) The impurity is also soluble in the solvent. This is obviously the case if the whole of the solid dissolves in the hot solvent. (The impurity may sometimes be insoluble in the hot solvent, in which case it can be removed by filtration of the hot liquid.)

The procedure is to dissolve the solid *completely* in the *minimum* amount of solvent, preferably at or near the boiling point, and then cool the liquid to about room temperature (a greater yield of recrystallised material can be obtained by cooling in ice). A single crystallisation can remove practically all the impurity if, when the solution is cold,

the amount of impurity present does not exceed its solubility value. Since it is not usually known whether this is the case, the purity of the recrystallised material is checked by a melting point determination on the dry solid (except in the case of salts, whose melting points are very high). If the solid melts sharply at a definite temperature, it is reasonably pure; if not, further recrystallisation is necessary until a sharp melting point is obtained.

8.5. The solubility of one liquid in another

When referring to a liquid, A, dissolving in another liquid, B, the terms *solute* and *solvent* cease to have any useful meaning and it is more usual to refer to the extent to which A and B will mix. Many pairs of liquids will mix in all proportions, for example ethanol and water (both strongly polar), and tetrachloromethane and benzene (both non-polar). Such pairs of liquids are said to be *completely miscible*. On the other hand, two liquids with very different intermolecular forces, such as a polar and a non-polar liquid, may have only a very small solubility in each other and are therefore only *partially miscible*.

Partial miscibility occurs in the case of methanol, which is polar, and cyclohexane, which is a non-polar hydrocarbon. If a small amount of methanol is added to some cyclohexane, it will dissolve completely to give a homogeneous mixture. As more methanol is added, a point will soon be reached where the solubility has been exceeded, and the methanol that cannot dissolve forms a separate liquid layer lying on top of the cyclohexane. The liquids are now partially miscible. The two layers are both saturated solutions, the top layer being a solution of cyclohexane in methanol, the lower layer a solution of methanol in cyclohexane. If the temperature is raised, the solubilities of each liquid in the other will increase, so that the upper layer will contain more cyclohexane and the lower layer more methanol. The solubilities at different temperatures can be shown in the form of a diagram by plotting the composition of the two layers against the temperature (Fig. 50). As the temperature is increased, the compositions of the two layers approach one another. At the maximum of the curve it is no longer possible for two layers to exist, since they would have the same composition. The temperature corresponding to the maximum is known as the *upper critical solution temperature* or CST, and above this temperature the liquids are miscible in all proportions. In some systems the mutual solubility increases again at a lower temperature, owing to association between the molecules of the two substances. There is then a lower critical solution temperature also, below which there is again complete miscibility.

If a mixture of the two liquids of composition *a* is shaken up, there will be two separate layers at any temperature below t_1 . At a temperature t_2 , for example, the layers will have the compositions *b* and *c*. On raising the temperature, the compositions of the two layers will change,

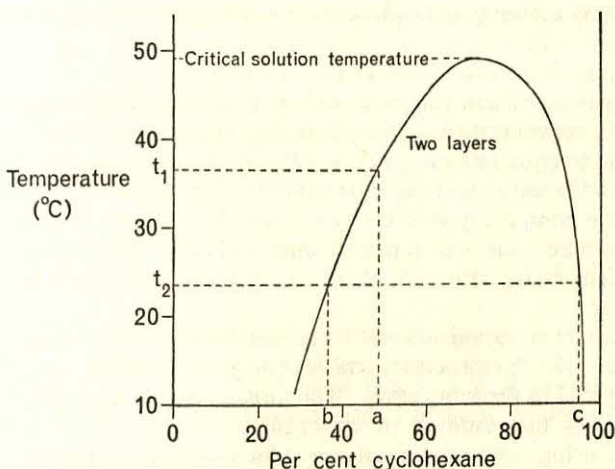


Fig. 50. Partially miscible liquids: methanol-cyclohexane

following the curve, until at t_1 one of the layers will disappear, leaving a single liquid phase.

A diagram of this sort is easily constructed by taking mixtures of two liquids in varying proportions, heating them until they become completely miscible, and then cooling slowly until the temperature is reached at which the second liquid phase just begins to appear. This gives a point on the curve for each mixture taken, providing it comes within the partially miscible region. The presence of two liquid phases is readily seen if the mixture is shaken or efficiently stirred, as one of the phases breaks up into small drops and causes the mixture to appear cloudy.

8.6. Distribution of a solute between partially miscible liquids

If a mixture of two partially miscible liquids, consisting of two layers as described above, has a third material dissolved in it, then this material will dissolve in each layer to an extent related to its solubility in that layer. At any one temperature, the concentrations of this material in the two layers will therefore be in a constant ratio. This is known as the *distribution law* (Nernst, 1891). It is often assumed, for the purpose of this relationship, that the two liquids are immiscible, in which case the law can be stated in the following way:

If a substance C is dissolved in a mixture of two immiscible liquids A and B, which are in equilibrium at a constant temperature, then

$$\frac{\text{Concentration of C in liquid A}}{\text{Concentration of C in liquid B}} = r,$$

where r is a constant which depends only on the temperature, and not

on the total amount of C present. r is known as the *distribution coefficient**.

The solute C may be either a solid, a liquid or a gas. The value of the distribution coefficient can be found by analysing the two liquid layers to find the concentration of the dissolved material, having first brought the system to equilibrium by keeping the mixture in a constant-temperature bath for a time with frequent shaking. The mixture is finally allowed to separate completely into the two liquid layers, and samples of both layers are taken out with a pipette and analysed. The result should be independent of the amounts of the two liquids, and of the solute, that were taken.

An important application of the distribution law occurs in the process of solvent extraction, which is of great value both in industrial processes and in the laboratory. The most common example of solvent extraction is the removal of an organic material from an aqueous solution, using an organic solvent which is almost immiscible with water (ethoxyethane, benzene, tetrachloromethane, etc.). If the distribution coefficient is large, a high proportion of the material can be extracted with a reasonable amount of solvent. Suppose an aqueous solution to have a volume V_1 and to contain m g of the material to be extracted. On shaking with a volume V_2 of an organic solvent, a certain proportion of the material will finally be dissolved in the solvent layer: let this proportion be x . Then in the solvent layer:

$$\text{Mass of solute} = mx$$

$$\begin{aligned}\text{Concentration of solute} &= \frac{\text{mass}}{\text{volume}} \\ &= \frac{mx}{V_2}\end{aligned}$$

In the aqueous layer:

$$\begin{aligned}\text{Mass of solute} &= m - mx \\ &= m(1 - x)\end{aligned}$$

$$\text{Concentration of solute} = \frac{m(1 - x)}{V_1}$$

The distribution coefficient is given by:

$$\begin{aligned}r &= \frac{\text{Concentration in solvent layer}}{\text{Concentration in aqueous layer}} \\ &= \frac{mxV_1}{m(1 - x)V_2}\end{aligned}$$

Hence

$$x = \frac{rV_2}{V_1 + rV_2}$$

* The term *partition coefficient* is sometimes used. It is not recommended owing to the possibility of confusion with the expression "partition function," which has a quite different meaning.

The proportion of material extracted is thus independent of the actual amount present, and is determined by the volume of solvent used relative to the volume of the aqueous solution, and the value of the distribution ratio. If successive extractions are made, using the same volume of solvent each time, the same proportion is removed in each extraction. It is more economical, when using a given volume of solvent, to make several extractions with small portions rather than one extraction with all the solvent at once: the following example illustrates this point.

EXAMPLE

The distribution coefficient for ethyl ethanoate between benzene and water is 12.2 at 20°C. If 1 dm³ of an aqueous solution containing 10 g of ethyl ethanoate is extracted with a total of 300 cm³ of benzene how much will be extracted (a) in a single extraction, (b) in three successive extractions of 100 cm³ each?

(a) Using 300 cm³ of solvent $V_2 = 300$ and $V_1 = 1000$.

$$\begin{aligned}\text{Proportion extracted} &= \frac{12.2 \times 300}{1000 + 12.2 \times 300} \\ &= \frac{3660}{4660} \\ &= 0.785\end{aligned}$$

$$\begin{aligned}\text{Mass extracted} &= 10 \times 0.785 \\ &= 7.85 \text{ g (i.e. 78.5\%)}\end{aligned}$$

(b) In the first extraction, using 100 cm³ of solvent, $V_2 = 100$ and $V_1 = 1000$.

$$\begin{aligned}\text{Proportion extracted} &= \frac{12.2 \times 100}{1000 + 12.2 \times 100} \\ &= \frac{1220}{2220} \\ &= 0.550\end{aligned}$$

$$\begin{aligned}\text{Mass extracted} &= 10 \times 0.550 \\ &= 5.50 \text{ g}\end{aligned}$$

$$\text{Mass left in aqueous layer} = 10 - 5.50 = 4.50 \text{ g}$$

The proportion extracted will be the same for all subsequent extractions if the volume of solvent used is the same as for the first:

$$\begin{aligned}\text{Second extraction} &= 4.50 \times 0.550 \\ &= 2.48 \text{ g}\end{aligned}$$

$$\text{Mass left in aqueous layer} = 4.50 - 2.48 = 2.02$$

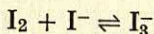
$$\begin{aligned}\text{Third extraction} &= 2.02 \times 0.550 \\ &= 1.11 \text{ g}\end{aligned}$$

$$\begin{aligned}\text{Total amount extracted} &= 5.50 + 2.48 + 1.11 \\ &= 9.09 \text{ g (i.e. 90.9\%)}\end{aligned}$$

The percentage extraction is thus 78.5% when all the solvent is used in one extraction, and 90.9% when it is taken in three separate equal portions.

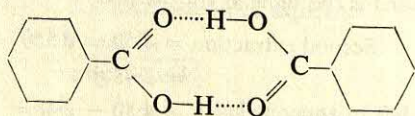
An important example of solvent extraction in industry is in the production of lubricating oils from residual petroleum oils. The latter are treated with a selective solvent such as liquid propane, which dissolves the lubricating oil portion (*i.e.* the more paraffinic portion), the asphalt and other undesirable constituents being much less soluble. Solvent extraction is also commonly used for the recovery of synthetic organic compounds, *e.g.* catechol and resorcinol are recovered from aqueous solutions by ether (ethoxyethane) extraction.

The distribution law is also extremely useful in investigating the equilibria that occur in ionic solutions when complex ions are formed. For example, iodine, which is not very soluble in water, dissolves readily in potassium iodide solution owing to the formation of a complex ion:



To investigate this equilibrium, it is necessary to find both the amount of free iodine (I_2) and also the amount that is combined in the complex ion I_3^- . The total iodine can be found by titrating the solution with thiosulphate(VI): as iodine is removed during the titration, the complex ion decomposes so that all the iodine is eventually titrated. To find the uncombined iodine, the solution is shaken with an organic liquid (*e.g.* tetrachloromethane). The iodine is distributed between the two liquids, but both the ionic forms remain entirely in the aqueous layer. A titration of the tetrachloromethane layer, together with the value of the distribution coefficient, will give the amount of molecular iodine in the solution.

The distribution law only applies to materials that are in the same molecular state in the two solutions, and so does not hold when the solute is largely dissociated or associated in one of the liquids. In some cases the law can be modified to allow for this, as in the case of carboxylic acids, which in benzene solution are almost entirely associated into double molecules owing to hydrogen bonding between the carboxylic groups, *e.g.* benzenecarboxylic acid:



In water, however, the acid is solvated, that is, the molecules are associated with water molecules rather than with each other. If some benzenecarboxylic acid is shaken up with a mixture of benzene and water until it has dissolved, it will be mostly in the form of single molecules in

the water and double molecules in the benzene. It can be shown that the distribution law will now take the form

$$\frac{\text{Concentration of benzenecarboxylic acid in water}}{\sqrt{(\text{Concentration of benzenecarboxylic acid in benzene})}} = \text{Constant}$$

8.7. The solubility of gases in liquids

The solubility of gases is usually small, except where there are strong attractive forces between the gas and solvent molecules or where chemical reaction occurs with the solvent. Thus the solubility of hydrogen, oxygen or nitrogen in water is very slight; ammonia, on the other hand, is very soluble largely because of the strong molecular attraction (hydrogen bonding) between ammonia and water. The solubility of a gas is also found to vary with the pressure. This is because the rate of dissolution of the gas molecules depends on the rate at which they strike the surface of the liquid, and therefore on the pressure of the gas (p):

$$\text{Rate of dissolution} = \text{Constant} \times p$$

The rate at which dissolved molecules escape from the liquid (*i.e.* evaporate) will be proportional to the concentration of the solution (c):

$$\text{Rate of evaporation} = \text{Constant} \times c$$

When the gas is in equilibrium with a saturated solution at constant temperature, these two rates will be equal, so that

$$c = kp$$

where k is a constant. This is a mathematical statement of *Henry's law* (1803), which states that *the mass of gas dissolved by a given volume of solvent at constant temperature is directly proportional to the pressure of the gas*. If there is only one gas present, p is the total pressure. Henry's law can also be applied to a mixture of gases, in which case p is the partial pressure of the gas being considered.

Since the pressure of a gas is proportional to the molar concentration, Henry's law can also be written

$$\frac{\text{Concentration of gas in the gas phase}}{\text{Concentration of gas in solution}} = \text{Constant}$$

which is another way of expressing the distribution law. The constant in this equation is, in fact, a distribution coefficient. It follows that Henry's law only applies to a substance that is in the same molecular form in the gas and in solution. This is particularly important in the case of gases which react with the solvent, *i.e.* the very soluble gases such as ammonia and hydrogen chloride, to which the law does not apply.

As quantities of gas are usually measured by volume, the solubility of a gas is normally expressed as *the volume of gas (measured at STP) dissolved by unit volume of solvent at a particular temperature, the gas pressure being 101.3 kPa*. This is known as the *absorption coefficient*. The following figures give the solubilities of several gases in water at 20°C:

Gas	He	H ₂	N ₂	O ₂	CO ₂	NH ₃	HCl
Absorption coefficient }	0.009	0.017	0.015	0.028	0.88	710*	442*

The figures for ammonia and hydrogen chloride (marked with an asterisk) were measured at 101 kPa pressure. Since Henry's law does not apply to these gases, these figures cannot be used to calculate the solubility at any other pressure.

The following example shows how the amount of gas dissolved by a certain volume of solvent can be calculated, using the absorption coefficient and Henry's law.

EXAMPLE

Hydrogen is shaken with 160 cm³ of water at 20° C and a pressure of 66.6 kPa. What mass of hydrogen will be dissolved?

The absorption coefficient is 0.017 at this temperature. 1 cm³ of water will therefore dissolve 0.017 cm³ of hydrogen (measured at STP) when the pressure is 101.3 kPa. For 160 cm³ of water:

Volume of hydrogen dissolved at 101.3 kPa = $0.017 \times 160 \text{ cm}^3$. Applying Henry's law:

$$\begin{aligned}\text{Volume of hydrogen dissolved at 66.6 kPa} &= 0.017 \times 160 \times \frac{66.6}{101.3} \\ &= 1.79 \text{ cm}^3 \text{ (at STP).}\end{aligned}$$

One mole of a gas occupies a volume of 22 400 cm³ at STP, and the relative molecular mass of hydrogen is 2.02. Hence:

$$\begin{aligned}\text{Mass of hydrogen dissolved} &= 2.02 \times \frac{1.79}{22\,400} \\ &= 1.61 \times 10^{-4} \text{ g}\end{aligned}$$

The calculation can be made in the same way for a mixture of gases, dealing with each gas separately in terms of its partial pressure.

EXAMPLE

When air is shaken with water at 20°C, what will be the percentage of nitrogen, by volume, in the dissolved gas?

Air contains 78% nitrogen by volume, and 21% oxygen. If the total pressure is p , the partial pressures are:

$$p_{\text{N}_2} = 0.78p \quad p_{\text{O}_2} = 0.21p$$

Taking the values for the absorption coefficients given above:

$$\text{Volume of N}_2 \text{ dissolved by unit volume of water} = 0.015 \times 0.78p$$

Volume of O_2 dissolved by unit volume of water = $0.028 \times 0.21p$

$$\text{Ratio of nitrogen to oxygen} = \frac{0.015 \times 0.78}{0.028 \times 0.21} = 2.0$$

There are thus 2.0 volumes of nitrogen to every one volume of oxygen, so that the percentage of nitrogen is

$$\frac{2.0}{3.0} \times 100 = 67\%$$

(Note that, since it is only a ratio of two volumes that is being considered, the temperature and pressure at which the volumes are measured does not matter, provided they are the same for both).

When molecules of a gas dissolve in a liquid, the process is similar to the condensation of a gas to a liquid, and therefore heat is evolved. Application of Le Chatelier's principle will show that the solubility will decrease as the temperature is raised. This is illustrated by the decrease in absorption coefficient: for CO_2 , for example, the value is 1.71 at $0^\circ C$ and 0.67 at $30^\circ C$.

This reduction in solubility means that if a liquid that is saturated with gas is heated, some of the gas is expelled: when water (which is normally saturated with air) is heated, bubbles of gas are seen to escape before the water actually boils. This behaviour can be put to practical use when it is desired to remove most of the dissolved gas from a liquid. In experiments where this is necessary, the liquid is boiled and is then practically free from dissolved gas.

Dissolved gas is also expelled when the pressure of the gas in contact with the liquid is reduced. An example of this is seen when a bottle of "fizzy" lemonade is opened; also the dissolved air in water will be vigorously expelled if the pressure is reduced with a water pump. Another way of reducing the pressure of gas in equilibrium with a liquid is to bubble a different gas through the liquid: the partial pressure of the dissolved gas is lowered and it is therefore expelled, to be carried away in the gas stream. The liquid will eventually be saturated with the gas that is bubbled through, the previously dissolved gas being completely removed. In this way water can be freed from oxygen by passing nitrogen through it, and the oxides of nitrogen that are usually present in nitric acid can be removed by bubbling air through the acid.

8.8. Determination of the solubilities of gases

The solubility of a sparingly soluble gas can be measured with the apparatus shown in Fig. 51. The volume of the bulb, A, is first found by filling it with water and running this out into a measuring cylinder. It is then refilled, this time with water that is gas-free. The gas whose solubility is to be determined is passed from a suitable generator or gas-holder into the gas burette, B, and the volume and temperature are noted. The two-way tap is then turned to connect B with A, both taps

of bulb A are opened, and about half the water in A is forced out under slight pressure and collected in a measuring cylinder. The lower tap of A is then closed, and the bulb immersed in a constant temperature bath, where it is shaken gently to speed up the attainment of equilibrium. More gas is admitted from B as the gas dissolves, to keep the pressure at the required value; if the latter is to be atmospheric pressure, the levels of the mercury in the burette are kept at the same height as shown in the diagram, but for any other pressure it is more convenient to connect

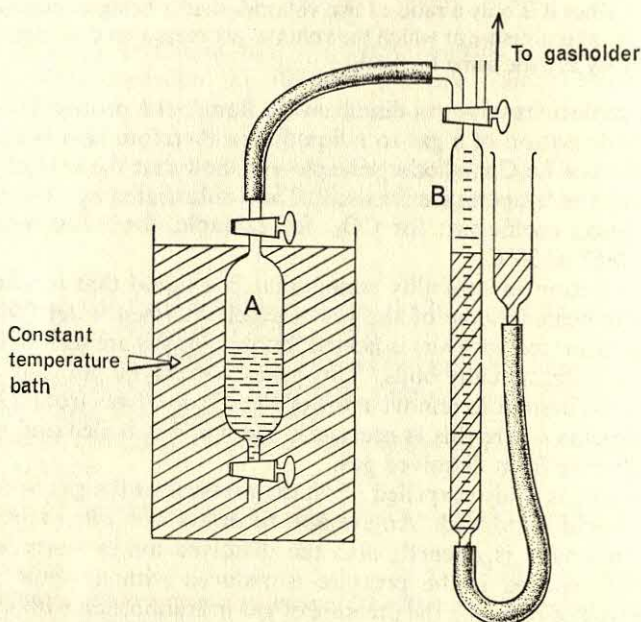


Fig. 51. Determination of the solubility of a sparingly soluble gas

a manometer to the tube leading to A. Equilibrium is reached when the volume reading on the burette remains constant (or, when a manometer is used, when the pressure reaches a steady value).

To calculate the absorption coefficient, it is necessary to know the following:

(a) *The volume of water in A.* This is equal to the measured volume of A, minus the volume of water run out at the start of the experiment.

(b) *The volume of gas dissolved,* measured at STP. This is found by subtracting the total volumes of gas in A and B (both corrected to STP) from the original volume of gas in B at the start, similarly corrected.

(c) *The pressure of the gas.* This is not equal to the total measured pressure, because water has an appreciable vapour pressure and the

gas in A is actually a mixture of the original gas and water vapour. The pressure required is therefore the partial pressure of the gas, which is equal to the total pressure minus the vapour pressure of water at the temperature of the bath.

From these figures, the volume of gas (measured at STP) that would be dissolved by unit volume of water at 101.3 kPa pressure can be calculated, using Henry's law.

In the case of very soluble gases, the volume of gas involved is very large, and it is more convenient to analyse the saturated solution by chemical means. The liquid is contained in a bulb (previously weighed empty) which is placed in a constant temperature bath (Fig. 52). The

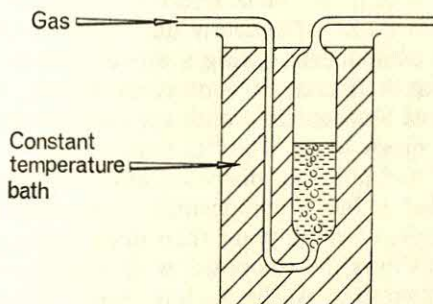


Fig. 52. Determination of the solubility of a very soluble gas

gas is bubbled through the liquid at a constant pressure, usually atmospheric. After allowing sufficient time for the solution to become saturated, both ends of the bulb are sealed off, and the dried bulb is weighed, together with the two end pieces. This gives the mass of the solution. The method of analysis depends on the chemical nature of the gas. In the case of ammonia, one end of the bulb would be broken under the surface of a measured volume of standard acid solution sufficient to neutralise all the ammonia, and the solution then washed out of the bulb. A titration of the excess of acid would then give the mass of ammonia in the solution. If the absorption coefficient was required, the mass (and hence the volume) of water could be found by subtracting the mass of ammonia from that of the solution, while the volume of ammonia at STP corresponding to the mass found could be calculated from the gas laws.

8.9. Solid solutions

It was stated in § 7.4 that when two substances are isomorphous (*i.e.* are very similar in crystalline form) they can crystallise together as a *homogeneous solid solution*. For example, silver and gold both have the same type of crystal lattice (face-centred cubic) and their atoms are

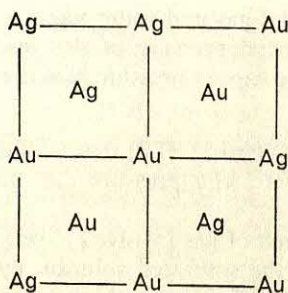


Fig. 53. Crystal lattice of a solid solution of silver and gold

of similar size. If the two metals are melted together and the mixture is allowed to cool, the crystals that form contain a homogeneous mixture of silver and gold (see Fig. 53). Other examples of pairs of substances that form solid solutions are salts that have ions of the same charge and similar size and structure (e.g. lead bromide and lead chloride), and molecular substances where both molecules are of similar size and structure (e.g. naphthalene and 2-naphthol).

The freezing points of solid solutions frequently lie between the melting points of the two pure components, giving a curve such as that in Fig. 54 marked "Liquidus." If a mixture of composition *a* is melted to a temperature t_1 and then cooled, solid will start to separate out when the temperature drops to t_2 . The "Liquidus" curve shows the composition of the liquid phase at this point, but if the solid is analysed it will be found that it has a composition *b*, containing more of the component of higher melting point than does the liquid. The lower, "Solidus", curve shows the composition of solid in equilibrium with liquid at any temperature. As the mixture cools from t_2 to t_3 , the composition of the liquid changes continuously from *a* to *c*, and the composition of the solid from *b* to *a*.

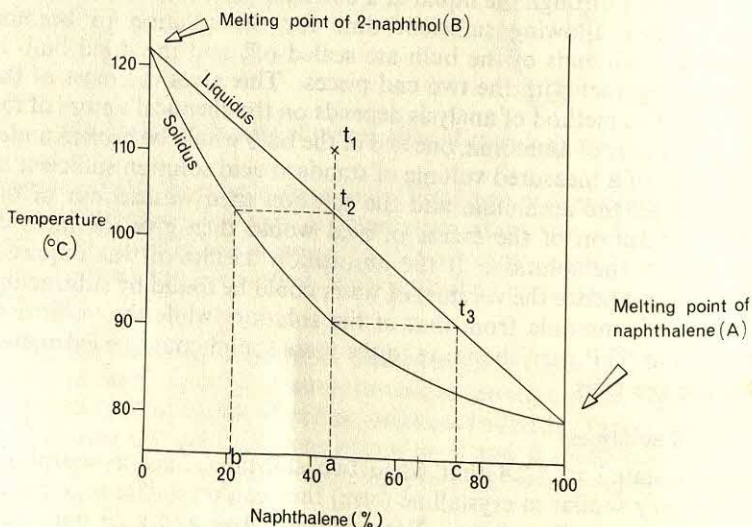


Fig. 54. Solid solution diagram for naphthalene and 2-naphthol

If the solid and liquid had been separated before solidification was complete, then the liquid would be richer in component A than was the original mixture, while the solid would be richer in component B. By repeating this process on the two separate fractions, further enrichment can be achieved and, with constant repetition, a complete separation of A and B is theoretically possible.

8.10. Immiscible solids

It is fairly uncommon for two substances to be completely miscible in the solid state, because the necessary similarity in size and crystal structure will not often occur. It frequently happens, therefore, that two substances which may be completely miscible when in the liquid state will not form solid solutions: if the liquid mixture is cooled, one or other of the two components will separate as the solid phase. In this case, it is found that the freezing point of either of the pure components is always lowered by the addition of the second component. In Fig. 55 the curves show the freezing points of mixtures of lead and antimony,

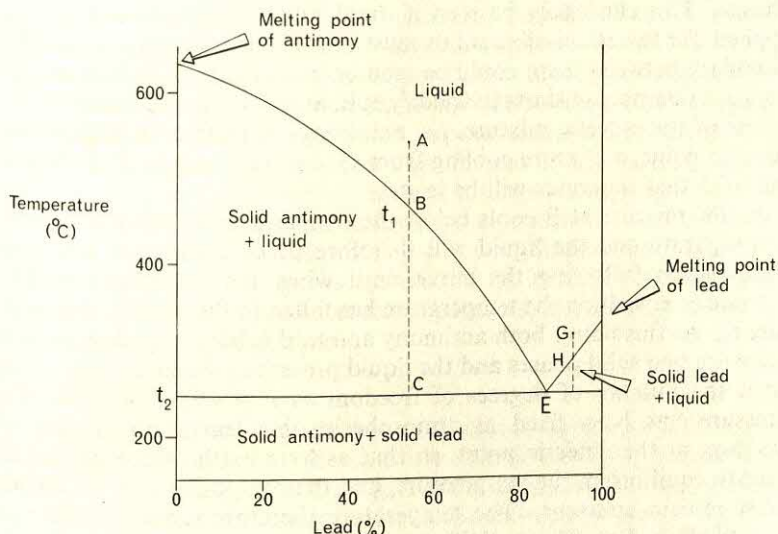


Fig. 55. Eutectic diagram for lead and antimony

and it will be seen that, starting from either pure lead or pure antimony, the freezing point decreases on the addition of the other component. The two curves meet at a point, E, which gives the lowest freezing point of any mixture of lead and antimony: a mixture of this composition is known as *eutectic* (Greek *eu-tektos*, "easily melted"). The temperature at which the eutectic mixture freezes is known as the *eutectic temperature*.

Above the curves, all mixtures are in the molten state, and since the two metals are completely miscible when liquid there is only one liquid phase. On cooling down a mixture from point A on the diagram, solidification will start when the temperature drops to t_1 , which is the freezing point of a mixture of this composition. At this point, liquid and solid must be in equilibrium, so that the phase rule may be applied. As there are two components, $P + F = C + 2$ becomes $P + F = 4$. The number of degrees of freedom F at point B can be found as follows. The position of B can be altered by varying either the composition or the temperature, but since B must lie on the curve only one of these can be varied independently. In addition, there is the effect of pressure: diagrams of this type are drawn for one particular pressure (usually atmospheric), so that the pressure is another independent variable. The total number of degrees of freedom is therefore two, and at point B the number of phases in equilibrium is given by $P = 4 - F = 2$. This means that, in addition to the liquid phase, there can be only one solid phase. Now, since the components are immiscible in the solid state, if both were present as solids at the same time there would be two solid phases. This can easily be seen if the definition of a phase (§ 7.9) is applied, for two immiscible solids must exist as separate crystals and the boundary between them could be seen on examination. It follows that only one component starts to solidify at B, and it will be the one that is in excess of the eutectic mixture, *i.e.* antimony. On the other side of the eutectic point, a mixture cooling from G will start to solidify at H and the solid that separates will be lead.

As the mixture at B cools below the temperature t_1 , more antimony will separate and the liquid will therefore become richer in lead, the composition following the curve until when the liquid reaches the eutectic composition the temperature has fallen to the eutectic temperature t_2 . At this point, both antimony and lead solidify together, so that there are two solid phases and the liquid present at the same time. This gives the number of degrees of freedom as $F = 4 - P = 1$. As the pressure has been fixed at atmospheric, this leaves no degrees of freedom at the eutectic point, so that as long as the three phases all exist in equilibrium the temperature, and the composition of the liquid, must remain constant. The temperature therefore remains steady at t_2 until all the liquid has solidified; as one phase has then been removed, the temperature can fall again as the solid mixture cools. A cooling curve starting with a molten mixture would therefore appear as in Fig. 56(a), unless the mixture had exactly the eutectic composition, when the temperature would remain constant as soon as solid started to separate, as in Fig. 56(b).

It follows that in the area under the left-hand curve in Fig. 55 only liquid and pure antimony can exist in equilibrium, while on the other side the solid will be pure lead. Below the eutectic temperature, the area represents a mixture of solid antimony and solid lead.

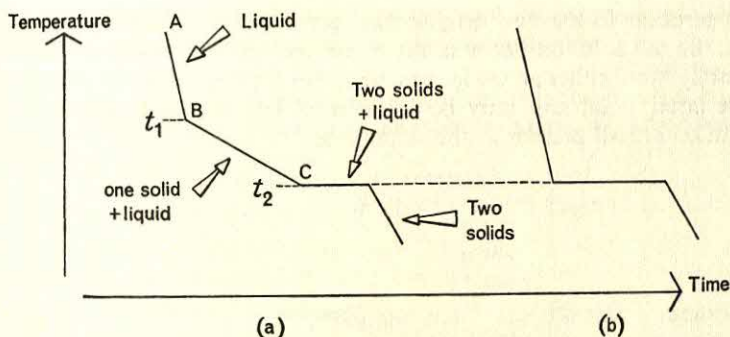


Fig. 56. Cooling curves for a eutectic system. (a) A mixture not of the eutectic composition; (b) The eutectic mixture

Eutectic diagrams are of importance in metallurgy, as for example in the production of low-melting alloys. Solder, which is a mixture of lead (melting point 326°C) and tin (232°C), melts at a temperature depending on the composition, the minimum being 183°C at the eutectic composition of about 62% lead. Many metal mixtures, however, result in more complicated diagrams owing to the formation of compounds.

Both molecular and ionic compounds may also show the same type of behaviour, and this explains why an impure material will not show a sharp melting point. Reference to Figs. 55 and 56 shows that when a mixture is heated it will begin to melt at a temperature t_2 but will not become completely liquid until a higher temperature t_1 is reached. t_1 will always be lower than the melting point of the pure substance.

The only exception to this is the case of the eutectic mixture itself, which melts sharply at the eutectic temperature, in fact in this respect it behaves like a pure substance.

8.11. Freezing mixtures

A special case of the eutectic type of system is when one of the components is water and the other a fairly soluble salt. As the melting point of a salt is usually very high, part of the diagram is usually omitted so that the region of the eutectic point can be shown with greater clarity: Fig. 57 shows the diagram for potassium chloride and water. The curve AB represents the freezing point of solutions of salt; the component which is in excess to the left of the eutectic point is water, so that the solid that separates in this region is ice. Curve BC shows the equilibrium between salt and solution: the solutions must therefore be saturated, and BC is the solubility curve for salt in water.

The practical importance of this diagram is that it shows that with suitable mixtures of ice, water and this salt, temperatures from 0°C to -11°C may be reached. Ice and water alone are in equilibrium at 0°C , but if salt is added some of the ice will melt in order to reduce the

temperature to the new equilibrium position. As more salt is added and the salt solution becomes more concentrated, the temperature falls steadily, until either all the ice has melted or the eutectic point is reached. The latter point can only be achieved if ice, salt and saturated salt solution are all present at the same time.

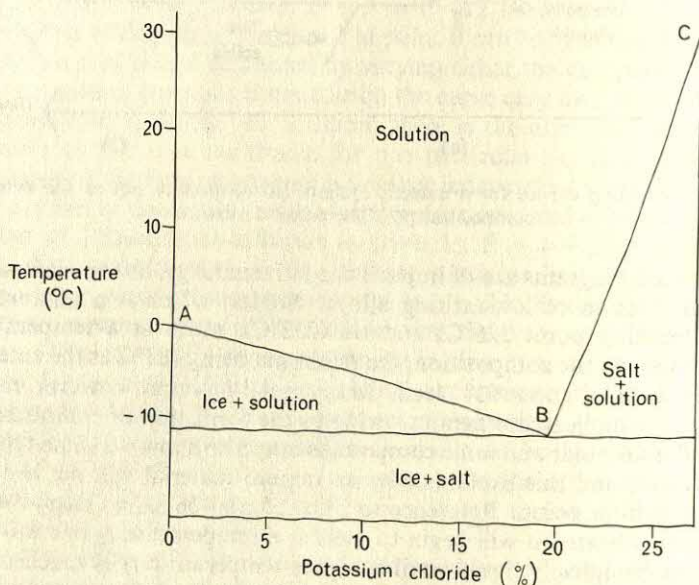


Fig. 57. A salt (potassium chloride) and water system

QUESTIONS

G.C.E.

1. Define, with reference to aqueous solutions of a solid, the terms *saturated solution*, *supersaturated solution* and *solubility*. Describe how to determine the solubility of hydrated ferrous sulphate ($\text{FeSO}_4 \cdot 7\text{H}_2\text{O}$) in water at 25°C , giving details of the analysis of the solution. Draw a rough diagram of the solubility curve of sodium sulphate and account for its abnormal shape. [Oxford]

2. Saturated solutions of sodium carbonate were prepared at different temperatures and 5 g samples of each solution analysed. The results are shown below:

Temperature ($^\circ\text{C}$)							
0	10	20	30	40	60	80	100
g Na_2CO_3 per sample							
0.33	0.55	0.89	1.38	1.61	1.58	1.58	1.56

Calculate the number of moles of sodium carbonate which will dissolve in 1000 g water at each temperature and use the figures to plot a solubility

curve. What can you deduce from your diagram? Suggest further experiments by which you would attempt to verify your deduction.

[C = 12; O = 16; Na = 23]

[Cambridge

3. The following results were obtained at equilibrium for the distribution of a weak organic acid when shaken with a mixture of water and carbon tetrachloride:

Concentration of acid in aqueous layer = c_1	Concentration of acid in tetrachloride layer = c_2
4.87	0.292
7.98	0.785
10.70	1.410

Calculate the ratios c_1/c_2 and $c_1/\sqrt{c_2}$ and state your conclusion regarding the molecular state of the acid in the tetrachloride layer. It may be assumed that the acid has a normal relative molecular mass in aqueous solution.

[London

4. Describe how you would determine the solubility of a gas in water. Assuming that, at 15°C and 101 kPa pressure, (a) air is a mixture of 80% N₂ and 20% O₂, (b) oxygen is twice as soluble in water as nitrogen, calculate the percentage, by volume, of oxygen in the gases boiled out from water which has stood for some time in contact with the atmosphere at 15°C.

[Cambridge

5. A solute S exists in the same molecular state when dissolved in ether and in water. When the two solutions are in equilibrium with each other, the concentration of the ethereal solution is 6.0 times that of the aqueous solution. A solution containing 14.0 g of S in 240 cm³ of water is extracted with one 40 cm³ portion of ether. The total mass of S extracted from the water will be

A 2.0 g B 6.0 g C 7.0 g D 12.0 g E 13.6 g [Cambridge

6. (a) State the law defining the equilibrium distribution of a solute between two immiscible solvents.

(b) (i) Outline the method you would use to determine the distribution coefficient of iodine between water and tetrachloromethane (carbon tetrachloride) at room temperature.

(ii) State how and why the distribution of iodine would be affected by the addition of potassium iodide to the aqueous layer in (i).

(c) Industrially, silver is extracted from molten lead using molten zinc which is insoluble in lead. The solubility of silver is 300 times greater in zinc than it is in an equal volume of lead. If 0.005 litre of molten zinc is added to a liquid solution of 2 g of silver in 0.1 litre of lead, calculate the percentage of silver extracted by the zinc when the system has attained equilibrium.

[A.E.B., 1977

7. There are a number of physical properties said to be characteristic of metals. List such properties and explain their origin so far as you can, using sodium (m. pt. 371 K) and copper (m. pt. 1356 K) as examples.

Copper and nickel form a complete series of solid solutions. Giving important practical details, outline how you could obtain a freezing point/composition diagram for the copper-nickel system.

[W.J.E.C.

8. Metal lattices are *close-packed*. Explain what is meant by this term, giving examples of **two** *close-packed* structures. Give **one** way in which a metal may not have a *perfect close-packed* structure. Describe the way in

which the atoms in a metal are held together, and show how its characteristic thermal, mechanical and electrical properties can be accounted for, using this description.

Tin and lead melt at 505 K and 600 K respectively. They form a single eutectic containing 63% tin, the eutectic temperature being 455 K. Use these data to sketch (roughly to scale) the tin-lead phase diagram, and use it to explain what happens when a molten mixture of 80% lead and 20% tin, which has a melting point of 550 K, is slowly cooled to room temperature.

[W.J.E.C.]

CHAPTER 9

PROPERTIES OF DILUTE SOLUTIONS

9.1. The vapour pressure of solutions

This chapter will be concerned with the vapour pressure of solutions and with certain properties which are directly connected with vapour pressure, *i.e.* boiling point, freezing point and osmotic pressure.

When a solution is made by dissolving a solid in a volatile solvent (*i.e.* in a liquid which has an appreciable vapour pressure), it can usually be assumed that the vapour pressure of the solid is so small that it can be ignored. The vapour pressure of the solution is therefore entirely due to the solvent, but it will be less than the vapour pressure of the pure solvent because of the presence of the solute molecules. We have already seen that the vapour pressure of a liquid results from an equilibrium between the rate at which molecules evaporate from the surface and the rate at which they condense from the vapour. In a solution, the number of solvent molecules at the surface is reduced (Fig. 58) and therefore the rate of evaporation is less than for the pure solvent: it is in fact reduced in proportion to the number of molecules of solvent compared with the total number of molecules (solvent plus solute) present. At equilibrium, the rate of evaporation is equal to the rate of condensation, and the latter is proportional to the vapour pressure, so that the vapour pressure of the solution (p) is related to the vapour pressure of the pure solvent (p^*) by

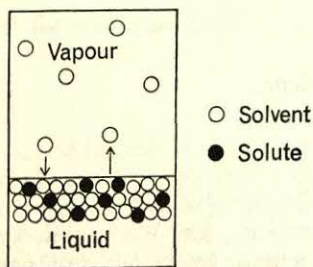


Fig. 58. Vapour-liquid equilibrium for a solution

$$p = p^* \times \frac{\text{Number of molecules of solvent}}{\text{Total number of molecules}}$$

and since we are dealing with a ratio, numbers of molecules can be replaced by number of moles.

When dealing with properties which depend on the relative numbers of moles of material present, it is convenient to express the concentration of a solution in terms of the *mole fraction* of the two components. Thus if the solution consists of n_2 moles of solute dissolved in n_1 moles of solvent, then the mole fractions x of the two components are

$$\text{Solvent: } x_1 = \frac{n_1}{n_1 + n_2}$$

$$\text{Solute: } x_2 = \frac{n_2}{n_1 + n_2}$$

It will be seen that $x_1 + x_2 = 1$; the total mole fraction of a mixture must always be equal to one.

We can now write

$$\begin{aligned} p &= p^\bullet \times \frac{\text{Number of moles of solvent}}{\text{Total number of moles}} \\ &= p^\bullet \frac{n_1}{n_1 + n_2} \\ &= p^\bullet x_1 \end{aligned}$$

The reduction in vapour pressure due to the presence of the dissolved material is given by:

$$\begin{aligned} \text{Lowering of vapour pressure} &= p^\bullet - p \\ &= p^\bullet - p^\bullet x_1 \\ &= p^\bullet (1 - x_1) \\ &= p^\bullet x_2 \end{aligned}$$

Hence

$$\frac{p^\bullet - p}{p^\bullet} = x_2$$

The quantity $(p^\bullet - p)/p^\bullet$ is known as the relative lowering of vapour pressure, and the equation above is a relationship discovered experimentally by Raoult (1887) and known as *Raoult's law*. It can be stated as follows: *the relative lowering of vapour pressure is equal to the mole fraction of the solute*.

It should be noted that the vapour pressure of a solution depends only on the relative number of molecules present and not on their chemical nature: physical properties of this type are known as *colligative properties*. In practice, it is found that this statement only holds good if the solution is dilute. In a concentrated solution the difference between the intermolecular forces of the solute and solvent molecules will cause a change in the attractive forces which solvent molecules have to overcome to escape from the liquid, and Raoult's law will not be obeyed. This may be regarded as non-ideal behaviour (just as in the case of a gas that does not obey the gas laws), and a solution is said to behave ideally if it obeys Raoult's law. At lower concentrations, the deviation from ideal behaviour becomes small. When applying Raoult's law, therefore, it must be stipulated that the solution concerned is dilute. This means that the number of moles of solute is small compared with

the number of moles of solvent, and may be ignored without great error. Raoult's law then takes the following approximate form:

$$\frac{p^{\circ} - p}{p^{\circ}} = \frac{n_2}{n_1 + n_2}$$

$$\approx \frac{n_2}{n_1}$$

i.e.

$$\text{Relative lowering of vapour pressure} = \frac{\text{Number of moles of solute}}{\text{Number of moles of solvent}}$$

9.2. Determination of relative molecular mass

From the measurement of a colligative property, the number of moles of solute present can be found. If the mass of solute is known, the relative molecular mass can therefore be calculated. If the solution contains m_2 g of solute dissolved in m_1 g of solvent, and the relative molecular masses are M_2 and M_1 respectively, then the numbers of moles are:

$$n_1 = \frac{m_1}{M_1} \quad n_2 = \frac{m_2}{M_2}$$

Substituting these values in the approximate form of Raoult's law,

$$\frac{p^{\circ} - p}{p^{\circ}} = \frac{m_2 M_1}{m_1 M_2}$$

In a solution of definite concentration, m_1 , m_2 and the relative molecular mass of the solvent M_1 will be known, so that the relative molecular mass of the solute can be calculated from the relative lowering of the vapour pressure.

One method of determining relative molecular masses would be to find the vapour pressure p° of the pure solvent and the vapour pressure p of a solution of known concentration. This method is seldom used, because the difference in vapour pressure is small and difficult to measure accurately.

In the *isopiestic* method (Greek, "equal pressure"), two solutions are used, one containing a known mass of the substance under investigation and the other a known mass of a reference substance dissolved in the same solvent. The solutions are placed in separate vessels inside a closed container which is maintained at a constant temperature. The principle of the method is that solvent will evaporate from the solution which has the higher vapour pressure, and the vapour will condense into the other solution. This will continue until both solutions have the same vapour pressure, i.e. they are isopiestic. The solutions are then analysed by weighing, the mass of solvent being found by subtracting the known mass of solute from the total mass. The vapour pressure of the reference solution can be calculated (because the relative mole-

cular mass of the solute is known) and this is equal to the vapour pressure of the other solution.

The isopiestic method is comparatively simple to carry out, but takes a long time (days or even weeks) during which time the temperature must be kept accurately constant. One application has been to substances of high relative molecular mass (up to 20,000), especially when other methods are unsuitable.

9.3. Boiling point elevation and freezing point depression

The vapour pressure of a solution will vary with temperature in a manner similar to that of the solvent, thus giving curves of the type shown in Fig. 59. The vapour pressure of the solution is always less

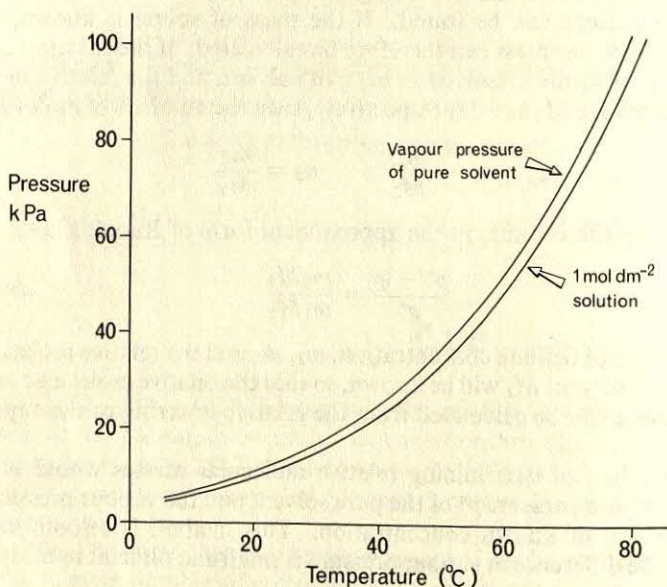


Fig. 59. Curves showing the lowering of vapour pressure of a solvent due to the presence of a non-volatile solute

than that of the pure solvent, but the difference decreases as the temperature is lowered (this is because $(p^* - p)/p^*$ is constant, so that $p^* - p$ is proportional to p^*). However, if the solution is dilute the two curves are close together and very nearly parallel.

Fig. 60 shows an enlarged picture of the vapour pressure curves in the region of the boiling point. The pure solvent boils at T_b , at which temperature its vapour pressure is equal to the atmospheric pressure. The vapour pressure of the solution does not reach this value until the higher temperature T , with the result that a solution always boils at a

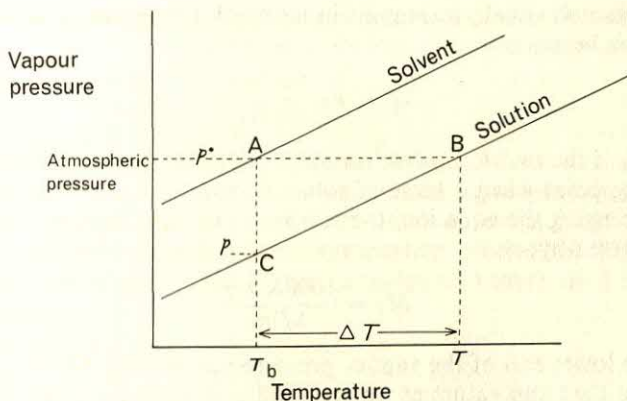


Fig. 60. Boiling point elevation of a dilute solution

higher temperature than the solvent. The boiling point elevation is given by:

$$\Delta T = T - T_b$$

To enable Raoult's law to be applied, ΔT must be connected with the relative lowering of vapour pressure. The vapour pressure of the solvent at its boiling point is p^* , while at the same temperature (T_b) the solution has a vapour pressure p , the lowering of vapour pressure ($p^* - p$) being equal to the line AC. ΔT is equal to the line AB. If the solution is dilute, the vapour pressure curves may be regarded as being approximately parallel straight lines over this very small section, in which case the ratio AB/AC will be constant for all such solutions. Hence:

$$\frac{\Delta T}{p^* - p} = \text{Constant}$$

$$\Delta T \propto p^* - p$$

and since p^* is a constant

$$\Delta T \propto \frac{p^* - p}{p^*}$$

but from Raoult's law

$$\frac{p^* - p}{p^*} = \frac{m_2 M_1}{m_1 M_2}$$

so that

$$\Delta T \propto \frac{m_2 M_1}{m_1 M_2}$$

When putting in the proportionality constant for this equation, the relative molecular mass of the solvent (M_1) can be incorporated. Since

the constant is usually expressed in terms of 1 kg of solvent, the final expression becomes

$$\Delta T = K_b \frac{1000m_2}{m_1M_2}$$

where K_b is the *molal elevation constant*, which is equal to the elevation of boiling point when 1 mole of solute is dissolved in 1 kg of solvent. On rearranging the equation, the relative molecular mass of the solute (M_2) is given by:

$$M_2 = \frac{1000K_b m_2}{\Delta T m_1}$$

At the lower end of the vapour pressure curves (Fig. 61) the solvent freezes at the temperature at which liquid and solid are in equilibrium, which corresponds with point D, where the vapour pressure curves for

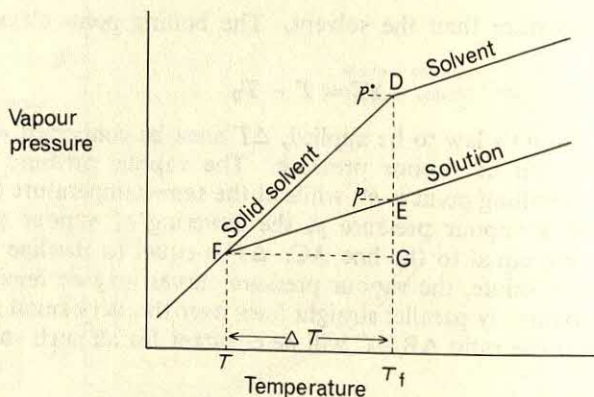


Fig. 61. Depression of freezing point of a dilute solution

solid and liquid meet (temperature T_f). The solution is also in equilibrium with solid solvent at its freezing point, so that the latter is at point F (temperature T). There is therefore a freezing point depression, given by:

$$\Delta T = T_f - T$$

If the vapour pressure of the solvent at its freezing point is p^* , and that of the solution at the same temperature is p , then $p^* - p$ is equal to DE , while ΔT is equal to FG . If, as before, it is assumed that for dilute solutions these small sections of the curves are parallel straight lines, then the ratios DE/FE and FE/FG are both constant for all solutions. It follows that DE/FG is constant, so that:

$$\Delta T \propto p^* - p$$

Proceeding in exactly the same way as in the case of the boiling point elevation, the following equation is obtained for the relative molecular mass of the solute:

$$M_2 = \frac{1000K_f m_2}{\Delta T m_1}$$

where K_f is the molal depression constant for 1 kg of solvent.

The constants K_b and K_f are characteristics of the particular solvent used, and can be calculated from relationships (derived from thermodynamics) which involve the specific enthalpy of vaporisation (Δh_v) or fusion (Δh_f):

$$K_b = \frac{RT_b^2}{1000\Delta h_v} \quad K_f = \frac{RT_f^2}{1000\Delta h_f}$$

R is the gas constant ($8.31 \text{ J K}^{-1} \text{ mol}^{-1}$), and T_b and T_f are the boiling and freezing points respectively, in kelvin. Values for the elevation and depression constants of some of the more commonly used solvents are given in Table 5.

TABLE 5. MOLAL DEPRESSION AND ELEVATION CONSTANTS

<i>Solvent</i>	<i>Freezing point (°C)</i>	K_f	<i>Boiling point (°C)</i>	K_b
ethanoic acid	16.7	3.90	118.1	3.14
propanone	—	—	56.2	1.72
benzene	5.5	5.12	80.1	2.57
camphor	179.5	37	—	—
trichloromethane	—	—	61.2	3.85
ethanol	—	—	78.4	1.20
water	0.0	1.86	100.0	0.51

It is essential that solvents used for relative molecular mass determinations should be as pure as possible. If the purity is in doubt, it is better to determine the constant experimentally by finding the depression (or elevation) caused by dissolving a known mass of a substance of known relative molecular mass. There is a further advantage to be gained by this procedure, for it can correct for experimental errors that are inherent in many of the methods used in determinations of relative molecular mass.

Methods for measuring freezing point depression and boiling point elevation will be described below, but since they all depend on the determination of small temperature differences, the measurement of the latter will be discussed first.

9.4. The measurement of small temperature differences

The magnitude of the boiling point elevation or freezing point depression depends on: (a) the value of the constant; (b) the concentration

of the solution; and (c) the relative molecular mass of the dissolved material.

The concentration is restricted by the fact that the equations used only apply to a dilute solution. For the highest accuracy, the amount of material dissolved per kg of solvent should not exceed 10 g, but in many cases (particularly with boiling point methods) the accuracy of the method itself is not great and a more concentrated solution (up to 100 g per kg of solvent) is permissible. Taking the smaller concentration, and imagining the solute to have a relative molecular mass of 100, the temperature difference calculated from the equation gives

$$\begin{aligned}\Delta T &= \frac{1000K \times 10}{100 \times 1000} \\ &= \frac{K}{10}\end{aligned}$$

As the constants vary between 0.5 and 5 (Table 5, excluding camphor), the temperature difference that has to be measured is a few tenths of a degree. To measure it to (say) 1% accuracy, the actual temperatures must be measured to a few thousandths of a degree.

The ordinary mercury-in-glass thermometer can be made sensitive to this extent, but in order to cover a reasonable temperature range the scale would have to be several yards long. Furthermore, it is only a temperature *difference* that is required: the actual boiling points (or

freezing points) of the solvent and solution need not be known. It was to meet this situation that a special type of thermometer was devised by Beckmann, designed to measure temperature differences on a scale covering only a few degrees, but which could be set so that the boiling point (or freezing point) of the solvent in use would fall within this temperature range. The modern version of the Beckmann thermometer is called a *differential thermometer* (Fig. 62) and usually has a scale calibrated from 0 to 6 degrees, sub-divided in $\frac{1}{100}$ degree. This scale measures temperature differences in kelvin, and when read to $\frac{1}{10}$ of a division with the aid of a lens will give an accuracy of 0.001. It should be noted that the figures on the scale do *not* represent degrees Celsius. The actual temperature corresponding to a particular reading depends on the amount of mercury in the bulb of the thermometer: by varying the amount, the temperature range can be altered at will. The adjustment is made by allowing mercury to run out of the bulb through the end of the capillary

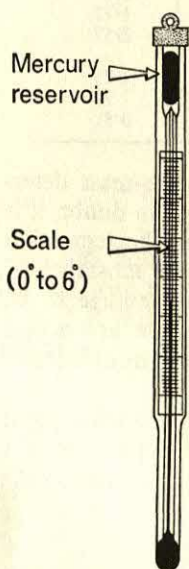


Fig. 62. Differential thermometer

tube (if the thermometer is to be set to record higher temperatures), or by returning some of the mercury from the reservoir at the top into the bulb if a lower temperature setting is required.

For solutes of high relative molecular mass (in the region of 1000 to 10 000) the temperature difference becomes so small that it is no longer possible to measure it with sufficient accuracy with a differential thermometer. Greater sensitivity can be obtained by using electrical methods of temperature measurement (*e.g.* thermocouples) and by this means relative molecular masses of up to 40 000 have been determined.

9.5. Measurement of boiling point elevation

In the boiling point method, the quantities to be determined are the boiling points of: (a) the pure solvent, and (b) a solution made by dissolving a known mass of the material in a known mass of solvent. The main practical difficulty lies in the fact that when liquids are boiled they superheat. The causes of superheating were discussed in § 6.5, where it was also explained that in the case of a *pure* liquid the true boiling point could be found by placing the thermometer in the vapour. This cannot be done in the case of a solution since the vapour from the boiling solution consists only of molecules of the solvent (the solute being assumed to be non-volatile). A thermometer in the vapour will therefore record the boiling point of the solvent and not that of the solution. It follows that the boiling point of a solution can only be measured by putting the thermometer bulb in the boiling liquid, so that it is essential to reduce superheating as much as possible. The accuracy of the method is limited by the extent to which this can be done.

Many different types of apparatus have been devised for reducing the superheating error, but the most widely used methods are based on a device introduced by Cottrell which allows the thermometer bulb to be above the surface of the boiling liquid and yet kept covered by a film of liquid which is pumped over it by means of a vapour pump (Fig. 63). When the liquid is boiling, bubbles of vapour rise from a metal wire sealed through the bottom of the vessel and force a stream of liquid and vapour up through the pump: this stream emerges from three jets above the thermometer bulb and keeps

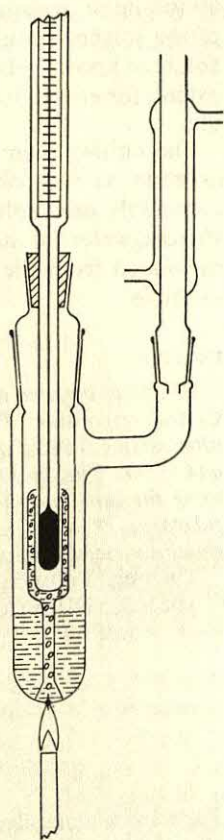


Fig. 63. Cottrell's apparatus for measuring elevation of boiling point

the latter continuously covered with liquid. The liquid and vapour come to equilibrium as they pass through the pump, and superheating is practically eliminated.

To carry out a determination, a known mass of solvent is introduced into the dry apparatus and boiled at a steady rate until the thermometer reading becomes constant: the figure is recorded as the boiling point of the pure solvent. Boiling is then interrupted while a known mass of solute is added through the side-arm. When boiling is resumed, the temperature will reach a new steady value, which is the boiling point of the solution. The condenser prevents loss of solvent during the experiment.

It is important that both temperatures should be measured within a reasonably short time, because of the variation of boiling point with atmospheric pressure. It is also desirable that the elevation constant of the solvent should be determined in a separate experiment, using a solute of known relative molecular mass. This compensates, to a certain extent, for errors due to superheating, solvent hold-up in the condenser, etc.

The boiling point method is quick, but the accuracy (1–5%) is not as good as that obtained in the freezing point method. The most commonly used solvents are benzene and propanone for organic substances, water for inorganic compounds. The relative molecular mass is calculated from the equation given above, as shown in the following example.

EXAMPLE

25 cm³ of benzene was used as solvent for a boiling point determination in a Cottrell apparatus. The readings on the differential thermometer, before and after adding 0.586 g of naphthalene (relative molecular mass 128), were 1.262 and 1.799. The density of benzene is 0.88 g cm⁻³. In a separate experiment, using the same amount of benzene but this time adding 0.627 g of an organic substance, Y, the temperature readings were 1.269 and 1.963. What is the relative molecular mass of Y?

The weight of solvent (m_1) is $25.0 \times 0.88 = 22.0$ g in each case.

The value of the elevation constant can be calculated from the first experiment, where $\Delta T = 1.799 - 1.262 = 0.537$.

$$\begin{aligned} K_b &= \frac{M_2 \Delta T m_1}{1000 m_2} \\ &= \frac{128 \times 0.537 \times 22.0}{1000 \times 0.586} \\ &= 2.58 \end{aligned}$$

The relative molecular mass of Y can now be calculated from the result of the second experiment, where

$$\begin{aligned} \Delta T &= 1.963 - 1.269 = 0.694. \\ M_2 &= \frac{1000 K_b m_2}{\Delta T m_1} \end{aligned}$$

$$\begin{aligned}
 &= \frac{1000 \times 2.58 \times 0.627}{0.694 \times 22.0} \\
 &= 106
 \end{aligned}$$

9.6. Measurement of freezing point depression

The freezing point of a solution can be measured with greater accuracy than the boiling point, because it is easy to keep the degree of supercooling low and a correction may be applied if high accuracy is required. Fig. 64 shows how the temperature of a solution alters as it is being cooled to below its freezing point. The true freezing point is at A, but owing to supercooling the temperature falls to B before solid starts to form. The temperature then rises rapidly to C, which is very close to the correct freezing point. The reason why C is slightly lower than A is that the solution is now more concentrated owing to the removal of some of the solvent by solidification. It is possible to apply a

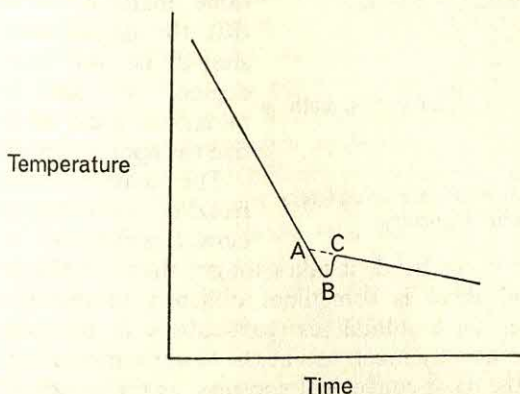


Fig. 64. Cooling curve showing supercooling of a solution

correction by extrapolating the cooling curve back to A as shown in the diagram, but this is not usually necessary as the amount of supercooling can be limited by (a) keeping the rate of cooling small, and (b) relieving supercooling by vigorous stirring or by seeding with small crystals of the solvent.

The apparatus used for freezing point measurements (Fig. 65) is based on Beckmann's original method. It consists simply of a tube with an air-jacket, which is immersed in a freezing bath, and a differential thermometer to measure the depression of the freezing point. The side-arm is provided for the addition of the solute. The air-jacket gives thermal insulation between the freezing bath and the inner tube, so that the rate of cooling can be controlled to a slow and steady rate.

A known mass of solvent is placed in the inner tube and the temperature of the freezing bath is adjusted to a few degrees below the freezing point of the solvent. The solvent is cooled to just above its freezing

point by immersing the inner tube directly in the bath, then the tube is replaced in the outer jacket and the temperature reduced to a little

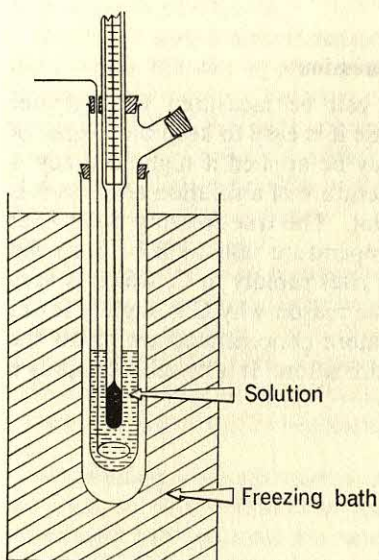


Fig. 65. Apparatus for measuring freezing point depression

below the freezing point; the liquid is then seeded by adding a small crystal of the solvent, when solid will separate and the temperature will rise. The maximum temperature is taken as the freezing point. The solvent is next warmed until the solid has all melted, and a weighed amount of solute is introduced through the side-arm and allowed to dissolve. The freezing point of the solution is then determined in exactly the same manner. It is important that the degree of supercooling should be not more than 0.5 degree, so that rough determinations must be made first to find the approximate freezing point.

The main advantage of the freezing point method is its accuracy, which can be better than

1%. On the other hand, it takes longer than a boiling point determination, and there is sometimes difficulty in dissolving sufficient of the solute, since solubilities (particularly in the case of organic materials) are usually much less at the lower temperature. Water and benzene are the most convenient solvents, as the freezing baths can be prepared from ice/water/salt mixtures (for water), or ice/water (for benzene). If the solvent is pure, it is not necessary to determine the depression constant: the value may be taken from tables.

EXAMPLE

When 0.703 g of yellow phosphorus was dissolved in 28.9 g of benzene, the freezing point was lowered by 0.995 degree. What is the relative molecular mass of phosphorus in benzene solution?

The value of K_f for benzene is 5.12.

$$\begin{aligned} M_2 &= \frac{1000K_fm_2}{\Delta Tm_1} \\ &= \frac{1000 \times 5.12 \times 0.703}{0.995 \times 28.9} \\ &= 125 \end{aligned}$$

As the relative atomic mass of phosphorus is 31.0, this must mean that in benzene solution the phosphorus exists as P_4 molecules.

9.7. Rast's freezing point method

It will be seen from Table 5 that camphor has the very high value of 37 for the freezing point depression constant. Molten camphor is a reasonably good solvent for many organic compounds, so that solutions containing 5–10% of solute can be used. The resulting depression of freezing point may be as much as 20 degrees, so that it is not necessary to observe temperatures to a greater accuracy than 0.1 degree and consequently an ordinary thermometer can be used. The determination of freezing point can be carried out by the conventional melting-point (capillary tube) technique, of which details were given above (p. 102). As this type of measurement requires only a very small amount of material, there is the added advantage that it is a semi-micro-method.

The melting point of the pure camphor is determined in the usual way. A small amount of the solute is then weighed out (only about 10 mg is required), about ten times the mass of camphor (accurately weighed) is added, and the mixture is melted in a stoppered or sealed tube (to prevent evaporation of camphor) and well mixed. After cooling, the solidified mixture is powdered and some of it placed in a melting point tube. The actual determination of freezing point differs somewhat from a normal melting point measurement, because the solid in this case is not a pure substance. For a mixture of two materials, there is a range of temperatures over which solid and liquid can be in equilibrium (see p. 129). The freezing point is the temperature at which solid first separates out when the molten mixture is cooled, or conversely if the solid is being heated it is the temperature at which the last trace of solid disappears. The temperature of the melting point bath is raised quickly until the solid in the capillary starts to melt, then more slowly as the solid gradually disappears. As the last trace vanishes the temperature is noted. There can be considerable personal variation in the determination; moreover the value of K_f shows appreciable differences between samples of camphor from different sources. Both these errors can be minimised by determining the value of the depression constant in a separate experiment, using naphthalene as the solute.

The advantages of Rast's method are that it is quick, needs no special apparatus, and requires only a small amount of material. On the other hand, the accuracy is not better than 5% and there are many substances that are not sufficiently soluble in camphor. Several other solvents with high depression constants are available, however.

9.8. Osmotic pressure

Fig. 66 illustrates the phenomenon of *osmosis*. An aqueous sugar solution is contained in a suitable membrane (e.g. a diffusion shell) to which a capillary tube is sealed, and the membrane is then immersed in water. The level of liquid in the tube will be found to rise, owing to flow of water into the solution; if the solution is dilute, the rise will slow

down and eventually stop. When this equilibrium position is reached, the solution is subject to a hydrostatic pressure due to the head of liquid. An analysis of the water would show that hardly any sugar had passed out through the membrane. Membranes that act in this fashion—allowing the solvent to pass through but not permitting passage of the solute—are said to be *semi-permeable*. The phenomenon of osmosis can be defined as *the flow of solvent into a solution (or from a more dilute to a more concentrated solution) when the two liquids are separated from each other by a semi-permeable membrane*.

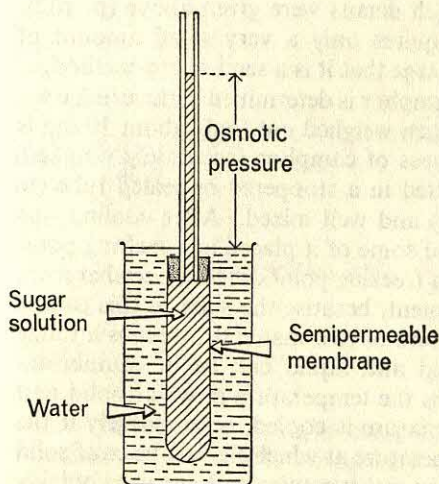


Fig. 66. Osmosis

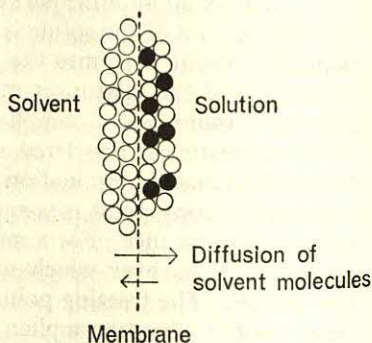


Fig. 67. How osmosis arises from the different rates of diffusion of solvent molecules through the membrane

A semi-permeable membrane must evidently contain minute pores through which the solvent molecules can travel. The membrane does not, however, act as a filter in the sense that the solute molecules are too large to pass through the pores, because osmosis can occur when both solvent and solute molecules are of comparable size. The most likely explanation is that the solvent molecules can attach themselves to the surface of the membrane by means of chemical bonds (hydrogen bonds play an important part here, especially when the solvent is water) and then work their way through the fine network of pores. This attachment of molecules to a solid surface is an example of the phenomenon of *adsorption*, which will be described in more detail later (§ 16.4). The reason why the solute molecules do not pass through the membrane is that they are not adsorbed on the surface of the membrane.

When the pressure on the two sides of a membrane separating a solution from the pure solvent is the same (Fig. 67), solvent molecules will diffuse through in both directions, but at different speeds, since the rate of diffusion in either direction will be proportional to the

concentration of the solvent molecules. There will therefore be a net transfer of solvent into the solution. In an apparatus such as that shown in Fig. 66 the resulting increase in the volume of the solution will cause a pressure to be developed, which will increase the rate at which solvent diffuses out of the solution. Equilibrium will eventually be reached when the two rates of diffusion are equal, and the pressure will then remain steady: this is the equilibrium osmotic pressure.

Materials which act as semi-permeable membranes include parchment, cellophane and copper(II) hexacyanoferrate(II). The latter material was used in the first quantitative experiments on osmotic pressure by Pfeffer in 1877 and is still one of the best membranes for aqueous solutions. Pfeffer prepared it by putting copper(II) sulphate solution on one side of a porous pot and potassium hexacyanoferrate(II) on the other, so that as the two solutions diffused into the pot they formed a precipitate of copper(II) hexacyanoferrate(II) inside the pores of the pot, the latter providing good mechanical support for the membrane.

Osmosis is a very important process in living organisms. Plant and animal cells contain, inside the cell wall, the cell fluid enclosed in a thin membrane. The membrane is largely semi-permeable and retains most of the dissolved material (salts, sugars, proteins, etc.) inside the cell, but allows the passage of water, substances necessary for the chemical reactions which take place in the cell (metabolism) and waste products. A cell will normally be surrounded by a solution of lower osmotic pressure than that of the solution it contains, so that water enters the cell and sets up an excess pressure, causing the membrane to be expanded against the cell wall. The cell is then said to be *turgid*. If, on the other hand, the cell was surrounded by a solution of high osmotic pressure (*i.e.* a concentrated solution), water would leave the cell and the membrane would shrink. In this condition the cell is said to be *plasmolysed*. By experimenting with solutions of different concentrations, it is possible to find the point at which the cell just fails to be plasmolysed. The solution is then *isotonic* with the cell fluid (Greek *iso-tonos*, "equal tension"), *i.e.* both solutions have the same osmotic pressure.

9.9. The measurement of osmotic pressure

Pfeffer's original measurements were carried out with an apparatus of the type shown in Fig. 68. The porous pot contains in its pores a copper ferrocyanide membrane, and is filled with a sugar solution. The pressure inside the cell is measured with a closed-end manometer containing air. The whole apparatus must be kept at constant temperature in a thermostat bath until the equilibrium pressure is attained, which may take several days.

The results of Pfeffer's work established the quantitative relationship between the osmotic pressure Π , the concentration of the solution c , and the temperature T (K):

(a) If the temperature is kept constant, the osmotic pressure is proportional to the concentration:

$$\frac{\Pi}{c} = \text{Constant}$$

(b) For a given concentration, the osmotic pressure is proportional to the absolute temperature:

$$\frac{\Pi}{T} = \text{Constant}$$

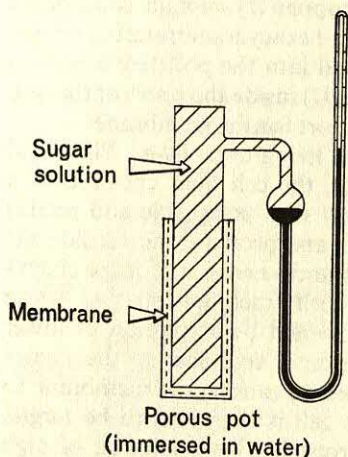


Fig. 68. Pfeffer's apparatus for measuring osmotic pressure (diagrammatic)

It was realised by van't Hoff that these laws were comparable with the laws governing the behaviour of gases. In the first law, for example, if c is the concentration in mol m^{-3} , then we can put $c = 1/V$, where V is the volume in m^3 containing one mole (*i.e.* the molar volume). We then have $\Pi V = \text{Constant}$, which is identical with Boyle's law. The second law is already identical with Charles's law.

If the two laws are combined, the result can be written

$$\Pi V = kT$$

and the value of the constant k can be found from osmotic pressure measurements: it is found that it is exactly the same as the gas constant

R , irrespective of the nature of the solution. The van't Hoff equation therefore becomes:

$$\Pi V = RT$$

or

$$\Pi = cRT$$

This equation is empirical, that is, it is based on experimental measurements and not on any theoretical reasoning, and it only applies accurately to very dilute solutions (less than about 0.1 mol dm^{-3}). However, for practical reasons, osmotic pressure measurements are usually made with dilute solutions, so that the van't Hoff equation can normally be used. One reason for avoiding strong solutions is that they give very high osmotic pressures, which are difficult to measure with accuracy.

EXAMPLE

What will be the osmotic pressure of a solution containing 9.94 g of sucrose (relative molecular mass 342) per dm^3 , at 7°C ?

The concentration of the solution is

$$c = \frac{9.94}{342} \times 1000 \text{ mol m}^{-3}$$

The value of the gas constant is $R = 8.31 \text{ J K}^{-1} \text{ mol}^{-1}$. The osmotic pressure will be given in Pa:

$$\begin{aligned} \Pi &= cRT \\ &= \frac{9.94}{342} \times 1000 \times 8.31 \times 280 \\ &= 67\,600 \text{ Pa} \end{aligned}$$

(Pfeffer's figure for this solution was 505 mm of mercury, which is $505 \times 133 = 67\,200 \text{ Pa}$).

One form of *osmometer* (an apparatus for measuring osmotic pressure) is shown in Fig. 69. The solution is contained in a small cylindrical glass cell, the ends of which are ground flat. A membrane is held against each end of the cell by means of a perforated stainless steel plate, the two plates being bolted together to make an effective seal. The area of membrane is large compared with the volume of solution, so that the time taken to reach equilibrium is reduced.

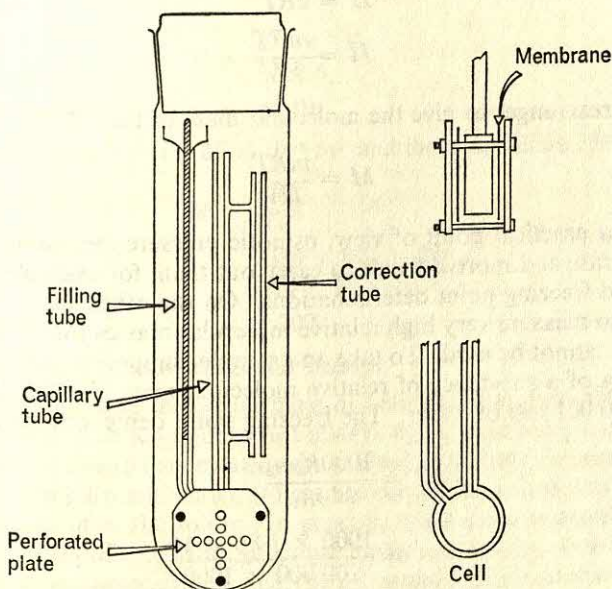


Fig. 69. Osmometer (Pinner-Stabin type)

The solution is introduced through the filling tube, which is then sealed. Sufficient of the pure solvent is put into the outer tube to immerse the cell completely, and the apparatus is then left in a thermostat bath until the height of solution in the capillary tube reaches a steady value. Part of the rise in the capillary tube is due to the surface tension of the liquid, and a correction is applied for this by having a length of identical tubing partly immersed in the solvent. The measured distance between the levels in the two capillary tubes gives the true osmotic pressure (since the solution is dilute, the surface tensions of solvent and solute are very nearly the same). Finally, the solution is removed from the cell and analysed to find the concentration. The latter is not quite the same as the original concentration, because during osmosis the solution becomes diluted with the amount of solvent that enters the cell to cause the rise in the capillary.

9.10. Relative molecular mass determination from osmotic pressure

Since the osmotic pressure of a solution depends on the molar concentration, such measurements can be used to determine the relative molecular mass of the solute. If a solution contains m g of a solute of relative molecular mass M in a volume of V m³, then

$$c = \frac{m}{VM}$$

and since

$$\Pi = cRT$$

$$\Pi = \frac{mRT}{VM}$$

and this rearranges to give the molecular mass of the solute:

$$M = \frac{mRT}{\Pi V}$$

From a practical point of view, osmotic pressure measurements are less accurate and more difficult to carry out than, for example, boiling point and freezing point determinations. On the other hand, they can be used to measure very high relative molecular masses for which other methods cannot be used. To take an example, suppose a solution contains 10 g of a substance of relative molecular mass 100 000 dissolved in 1 kg (0.001 m³) of water. The freezing point depression would be:

$$\begin{aligned}\Delta T &= \frac{1000K_f m_2}{M_2 m_1} \\ &= \frac{1000 \times 1.86 \times 10}{100\,000 \times 1000} \\ &= 0.00019\end{aligned}$$

This difference in temperature is far too small to measure accurately, so that the freezing point method would be useless. The osmotic pressure of the solution at 25°C would be:

$$\begin{aligned}\Pi &= \frac{mRT}{VM} \\ &= \frac{10 \times 8.31 \times 298}{0.001 \times 100\,000} \\ &= 248 \text{ Pa} \\ &= \frac{248}{133} \times 13.6 \text{ mm of water} \\ &= 25 \text{ mm}\end{aligned}$$

The rise in the capillary tube of the osmometer would therefore be 25 mm (for a dilute solution, the density of the solution is very nearly equal to the density of water). This height can be measured accurately, so that osmotic pressure measurements can be used to determine the relative molecular mass of polymers and other substances of high relative molecular mass.

EXAMPLE

A solution containing 0.380 g of a protein in 25 cm³ of aqueous solution gave an osmotic pressure of 62.4 mm (of solution) at 25°C. What is the relative molecular mass of the protein?

The osmotic pressure is:

$$\begin{aligned}\Pi &= \frac{62.4 \times 133}{13.6} \\ &= 610 \text{ Pa}\end{aligned}$$

The volume of solution is $25 \times 10^{-6} \text{ m}^3$, and the temperature 298 K.

$$\begin{aligned}M &= \frac{mRT}{\Pi V} \\ &= \frac{0.380 \times 8.31 \times 298}{610 \times 25 \times 10^{-6}} \\ &= 61\,700\end{aligned}$$

9.11. Abnormal relative molecular masses

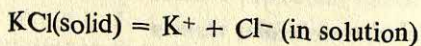
When the relative molecular mass of a substance is measured in solution, the value obtained does not always agree with the normal value. This may be due to (a) deviation from ideal behaviour (*i.e.* the solution does not obey Raoult's law), (b) association of the solute molecules, or (c) dissociation of the solute. In general, when there is *association* the solute consists of a mixture of single molecules, double molecules and possibly larger associations, and the measured relative molecular mass (which is the average value) is therefore greater than normal; whereas

dissociation, which occurs in electrolytic solutions, causes the solute to be split up into smaller particles (ions) and the measured relative molecular mass is less than the normal value.

Association in solution can be caused by hydrogen bonding between solute molecules, and is therefore observed in the case of compounds capable of forming such bonds, *e.g.* alcohols, phenols and carboxylic acids (*see* § 5.10 for similar behaviour in the gas phase). The extent of association is, however, also influenced by the nature of the solvent, as will be seen from the following example. The relative molecular mass of ethanoic acid, as determined by measurements in benzene solution, is almost exactly 120. This is just twice the normal value, and shows that the ethanoic acid molecules are almost entirely associated into double molecules (*see* p. 120 for the arrangement of the hydrogen bonds between associated carboxylic acid molecules). In aqueous solution, on the other hand, ethanoic acid gives the normal relative molecular mass of 60. This is because water molecules can associate with ethanoic acid molecules even more readily than the acid molecules associate with each other. It might be thought that association between solute and solvent would still cause the observed relative molecular mass to be greater than normal, but this is not so because Raoult's law is only concerned with the *number* of solute molecules compared with the total number of molecules; in this case the former is unaltered, while in a dilute solution the decrease in the latter is negligible. Solvents which prevent association of the solute are those that can themselves take part in hydrogen-bonding, *e.g.* water and alcohols.

In the case of other compounds that associate in solution (*e.g.* alcohols and phenols) the bonding is not so strong as it is for carboxylic acids, but on the other hand it is not limited to the formation of double molecules. The observed relative molecular mass therefore increases with concentration, and may vary from a little more than the normal value to several times the latter figure.

Solutions of strong electrolytes (*e.g.* strong acids, strong bases and salts) are found to give relative molecular masses that are much less than the normal value for the solute. This is because they are dissociated into ions: for example, potassium chloride in aqueous solution is dissociated into separate potassium and chloride ions:



As the solid potassium chloride is already ionic, this equation represents the splitting up of the solid into separate particles by the process of solution. In theory, the relative molecular mass in solution should be the mean of the relative molecular masses of the two ions, which is equal to exactly half the relative molecular mass of KCl. In practice, the freezing point depression of a 0.1 mol dm^{-3} solution of potassium chloride gives a relative molecular mass of 40.3, the theoretical value being $74.6/2 = 37.3$. The difference between these two figures is due to

the special nature of the attractive forces in ionic solutions, the electrical attraction between oppositely charged ions being much stronger than the normal forces of intermolecular attraction. This causes, firstly, deviation from Raoult's law on which the relative molecular mass determination is based. Secondly, the electrical forces may hold some of the ions together in pairs, each *ion-pair* consisting of one positive and one negative ion. The majority of electrolytes are incompletely dissociated owing to ion-pairing, but a small number of salts (including the alkali metal halides) are completely dissociated into separate ions. When an electrolyte solution is diluted, the average distance between the ions increases and the attractive forces therefore become less important: in very dilute solutions the observed relative molecular mass tends towards the theoretical (completely dissociated) value.

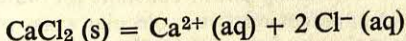
A useful way of expressing the extent of association or dissociation is by means of the van't Hoff *i* factor:

$$i = \frac{\text{Normal relative molecular mass}}{\text{Observed relative molecular mass}}$$

Association gives values of *i* less than unity, dissociation greater than unity. For example, from the figure given above for the observed relative molecular mass of a 0.1 mol dm⁻³ solution of KCl,

$$\begin{aligned} i &= \frac{74.6}{40.3} \\ &= 1.85 \end{aligned}$$

In more dilute solutions of KCl, the value of *i* tends towards a limiting value of 2, which is what would be expected of a solution that obeys Raoult's law and where the electrolyte is dissociated into two ions. A solution of a salt that gives three ions, *e.g.* calcium chloride,



will have a limiting *i* factor of 3, but again the actual value will always be less than this due to incomplete dissociation (ion-pairing) and deviation from Raoult's law.

QUESTIONS

G.C.E.

1. (a) The elevation in boiling point of a solvent by a solute is known as a *colligative property*. What is meant by this term? Give **two** other examples of colligative properties.

(b) How would you determine the molar mass of a compound in a named

solvent by an experiment involving one of these properties? Give concise experimental details.

(c) State, with reasons, why measurement of the elevation of boiling point could be used with an aqueous solution, to obtain the molar mass of urea (carbamide), but not ethanoic (acetic) acid.

(d) A solution of 2.8 g of cadmium iodide (CdI_2) in 20 g of water boiled at a temperature which was 0.20 K higher than the boiling point of pure water under the same conditions of pressure. Calculate the molar mass of the solute, and comment on the result. (The boiling point elevation constant for water is 0.52 K kg/mol.) [A.E.B., 1978]

2. (a) Assuming that the vapour pressure of water at any constant temperature is reduced on adding an involatile solute such as sugar by an amount proportional to the concentration of the solute, show with the aid of a diagram that the elevation of the boiling point of such a solution is proportional to the concentration of the solute.

(b) Give a labelled sketch of the apparatus you would use to determine the depression of the freezing point of a solution of sugar.

(c) The freezing point of pure benzene is 5.533°C . The freezing point of a solution of 15.25 g of benzoic acid, $\text{C}_7\text{H}_6\text{O}_2$, in 1000 g of benzene is 5.175°C , while that of a solution of 6.40 g of naphthalene (C_{10}H_8) in 1000 g of benzene is 5.277°C . What conclusions can you draw from this information?

[Oxford]

3. Describe how you would determine the relative molecular mass of a solute by measuring the depression in freezing point of water. State clearly the precautions you would take to ensure accuracy.

When 0.775 g of white phosphorus was dissolved in 50.0 g of benzene, the solution froze at 4.89°C . What value do these data give for the relative molecular mass of white phosphorus? What explanation can you offer for this value? [Freezing point of pure benzene = 5.53°C . Cryoscopic (freezing point) constant for benzene = $5.12^\circ\text{C mol}^{-1}$ kg, i.e. $5.12^\circ\text{C mol}^{-1}$ for 1000 g of solvent.]

[Cambridge]

4. An organic acid **W** has the empirical formula $\text{C}_7\text{H}_6\text{O}_2$. A solution of 2.56 g of **W** in 100 g of water has a freezing point 0.390 K below that of pure water. [The cryoscopic (freezing point) constant for water is 1.86 K mol^{-1} kg.] (a) Calculate the apparent relative molecular mass of **W** in water. (b) What is the apparent molecular formula of **W** in water?

A solution containing 4.63 g dm^{-3} of **W** in benzene exerts an osmotic pressure of 46.2 kPa (0.456 atm) at 293 K. [The gas constant $R = 8.31 \text{ J K}^{-1} \text{ mol}^{-1} = 0.0821 \text{ atm dm}^{-3} \text{ K}^{-1} \text{ mol}^{-1}$. $1 \text{ kPa} = 1 \text{ kN m}^{-2}$.] (c) Calculate the apparent relative molecular mass of **W** in benzene. (d) Explain your results in (a), (b) and (c) in terms of molecular structure and bonding. [Cambridge]

5. A solution of 2.00 g of a polymer in 1.00 dm^3 of water was found to have an osmotic pressure of 273 N m^{-2} at 0°C . Calculate to two significant figures the relative molecular mass (molecular weight) of the polymer. [Oxford]

CHAPTER 10

DISTILLATION

10.1. The vapour pressure of mixtures of miscible liquids

The process of distillation, which is the most useful method for separating liquid mixtures, consists of vaporising the liquid by boiling and then condensing the vapour. If the distillate (*i.e.* the condensed vapour) has a composition that is different from the original liquid, then some degree of separation will have been achieved. For this to be so, the boiling liquid and its vapour must differ in composition.

If a mixture of two liquids behaves in an ideal manner, *i.e.* if Raoult's law is obeyed, then each component will exert a vapour pressure in proportion to its mole fraction in the mixture (*see* § 9.1). Suppose the mixture to consist of n_A moles of a liquid A and n_B moles of another liquid B, and that the vapour pressures of A and B in the pure state are $p_A^\bullet$ and $p_B^\bullet$ respectively. The partial pressures of A and B in the mixture will be given by

$$p_A = p_A^\bullet \frac{n_A}{n_A + n_B}$$

$$= p_A^\bullet x_A$$

and similarly

$$p_B = p_B^\bullet x_B$$

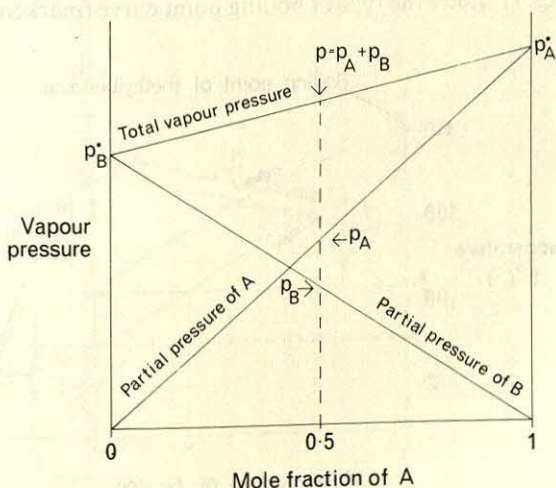


Fig. 70. Vapour pressures of a mixture of two liquids A and B

where x_A and x_B are the mole fractions of A and B in the mixture. At any particular temperature, p_A^* and p_B^* will be constant and the partial pressures of A and B will vary in proportion to their mole fractions. Fig. 70 illustrates this, and shows that the total vapour pressure of the mixture (p) also varies linearly with the molar proportions of A and B. The total pressure is equal to the sum of the two partial pressures:

$$p = p_A + p_B$$

Mixtures which behave ideally over the whole concentration range are uncommon, since this will only occur when the two liquids have similar intermolecular forces, *i.e.* their molecules must be similar in structure and size. Benzene and methylbenzene, methanol and water, are examples of pairs of liquids that are nearly ideal in behaviour.

Consider a mixture of equal numbers of molecules of A and B, as shown by the dotted line on the diagram at a mole fraction of 0.5. For this mixture the partial vapour pressure of A is greater than that of B: the vapour therefore contains more molecules of A than B, in other words the vapour is richer than the liquid in component A. The same is true for any other composition, and as A is the liquid with the higher vapour pressure the general conclusion can be drawn that *the vapour always contains more of the component with the higher vapour pressure than does the liquid*.

10.2. Distillation

A mixture of two liquids will boil when the total vapour pressure is equal to the external pressure, which is usually atmospheric. This means that the boiling point will vary with the composition of the mixture. Fig. 71 shows the type of boiling point curve (marked "Liquid")

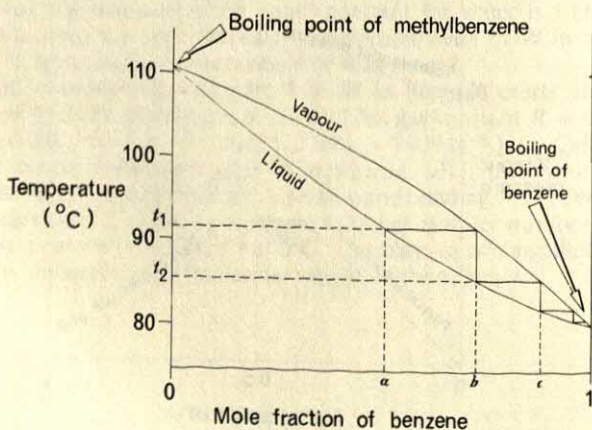


Fig. 71. Boiling point diagram for benzene-methylbenzene

given by an almost ideal mixture. To complete the diagram, the composition of the vapour obtained when the liquid is boiled is shown by means of a second curve (marked "Vapour").

If a mixture of composition a is heated, it will boil at a temperature t_1 . The composition of the vapour at this temperature will be at b , and when the vapour is condensed the distillate will have the same composition. It will be seen that, in accordance with the conclusion reached in the previous section, *the distillate is richer in the component with the lower boiling point (i.e. higher vapour pressure)*. As the distillation proceeds, the boiling liquid will become richer in the higher boiling component, so that the temperature will rise continuously. At the same time the composition of the distillate will also alter, following the vapour curve. A simple distillation will therefore only give a partial separation of the two liquids.

A much more effective separation is obtained by *fractionation*. If a small amount of distillate from the mixture boiling at t_1 was collected (having the composition b on the diagram), and this fraction again distilled, then at a temperature t_2 it would boil to give a distillate with composition c . If the process was repeated, the distillate would become continuously richer in component A, each separate distillation corresponding to one "step" on the boiling point diagram. After a definite number of such steps, pure A would be obtained. It would, in fact, be impracticable to fractionate a mixture by collecting distillates and re-distilling, because a very large number of separate distillations would have to be carried out in order to obtain any appreciable yield of pure

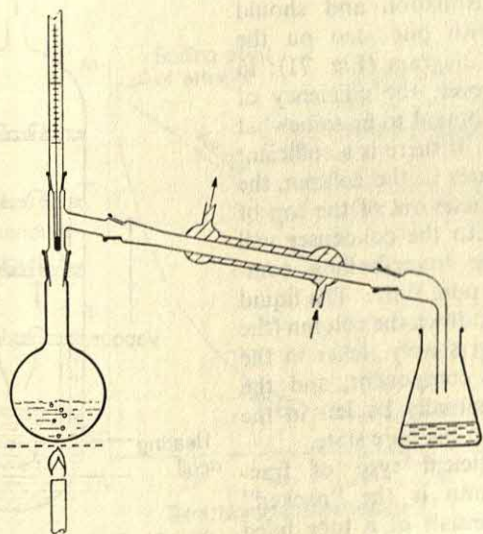


Fig. 72. Distillation apparatus

liquid, but the same result can be obtained in one operation by using a *fractionating column*, which will be described later.

Even in the simple form of distillation apparatus (Fig. 72) some fractionation takes place, owing to the liquid that condenses on the walls of the flask and partly vaporises again. Liquids that differ widely in boiling point can be separated more or less completely by a single distillation, depending on the actual difference in boiling point: an example is the removal of a low-boiling solvent such as ethoxyethane (35°C) from a high-boiling compound such as phenylamine (184°C). When a liquid is purified by distillation, it is usually found that the temperature does not remain constant at the true boiling point of the liquid, but continues to rise slowly: this is because separation is not quite complete. The fraction that boils over a small temperature range around the correct boiling point is collected and the actual temperatures are noted, since this gives a measure of the purity of the product.

Much more efficient separation is obtained by the use of a fractionating column. The way in which such a column operates is best illustrated by the type known as a "bubble cap" column (Fig. 73); it consists of a long tube divided into a number of separate compartments. The vapour rising from the boiling liquid passes into the first compartment (or *plate*), and some will condense there. The liquid lying on the first plate will therefore be richer in the component of lower boiling point. The hot vapour will now bubble through this liquid, causing it to boil, and the vapour passing into the second compartment will be still richer in the lower-boiling component. In theory, each plate is equivalent to a separate distillation and should correspond with one step on the boiling point diagram (Fig. 71); in practice, however, the efficiency of the column is bound to be somewhat less than that. If there is a sufficient number of plates in the column, the vapour that passes out of the top of the column into the condenser will consist of the lower-boiling component in the pure state. The liquid that runs back down the column (the *reflux*) is progressively richer in the higher-boiling component, and the latter will eventually be left in the boiler almost in the pure state.

Another efficient type of fractionating column is the "packed" column. It consists of a tube filled with small rings or coils made of

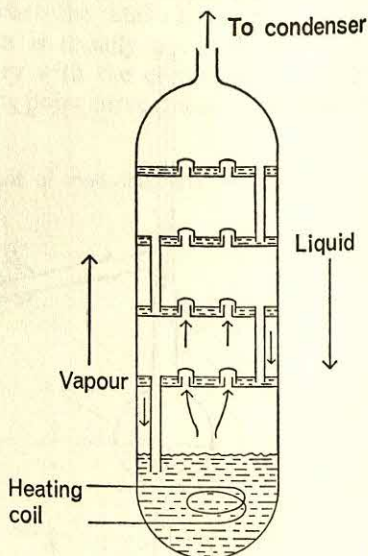


Fig. 73. Bubble-cap type of fractionating column

metal, glass or porcelain. This provides a large surface on which vapour can condense, while at the same time allowing continuous channels through which the vapour can pass. A packed column operates on exactly the same principle as a plate column, by bringing the vapour passing up the column into contact with the reflux liquid running down. The efficiency of a packed column is measured in terms of the length of column that is equivalent to one step on the boiling point diagram. This is known as the HETP (height equivalent to one theoretical plate).

10.3. Azeotropic mixtures

When the two liquids in a mixture differ markedly in their intermolecular forces, the vapour pressures will deviate appreciably from the ideal (Raoult's law) relationship shown in Fig. 70. This will happen when one liquid is much more polar than the other, for example in a mixture of an alcohol (highly polar) with a hydrocarbon (non-polar). The partial vapour pressures are then found to be greater than predicted by Raoult's law, and if the deviation is large enough the total vapour pressure curve will rise to a maximum—*i.e.* there will be a certain composition where the vapour pressure is greater than that of either of the two components. Such a mixture will therefore have the lowest boiling point, and the boiling point diagram will be of the type shown in Fig. 74.

The boiling point of a mixture of composition *a*, corresponding to the minimum of the curve, is lower than that of any other mixture or of either of the pure components. It will also be seen that the liquid and

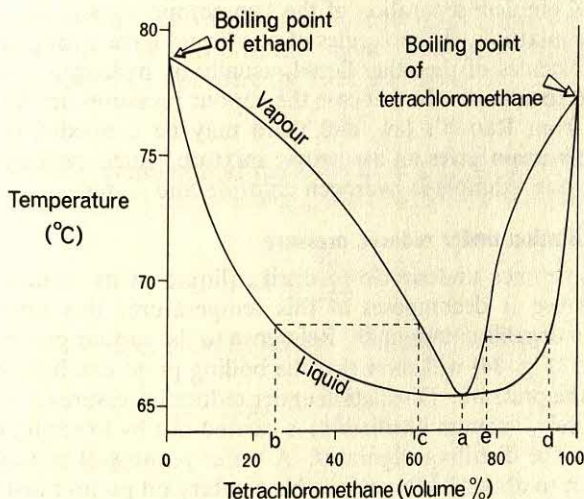


Fig. 74. Boiling point diagram for an azeotropic system (ethanol-tetrachloromethane)

vapour curves coincide at this point, so that if this mixture is boiled the vapour will have the same composition as the liquid. Such a mixture is known as an *azeotropic mixture* (Greek *a-zeo-tropos*, "to boil without change") or a *constant boiling mixture*. If an azeotropic mixture is distilled, the boiling point remains constant and the composition is unchanged. In this respect it behaves as though it were a pure substance, but it could be distinguished from the latter in the following way. The boiling point diagram (Fig. 74) refers to one particular pressure: if the pressure is altered, the azeotropic composition will also alter. A mixture that is azeotropic at one pressure will therefore lose its azeotropic properties if the pressure is changed. Examples of azeotropic mixtures are tetrachloromethane (boiling point 76.8°C) and ethanol (78.5°C), which give a minimum boiling point of 65.0°C ; and the ethanol-water system, with boiling points of 78.5°C and 100.0°C respectively, which gives an azeotropic mixture containing 95.6% by weight of ethanol which boils at 78.15°C .

The result of distilling mixtures of liquids which give a minimum boiling point can be seen by reference to Fig. 74. If a mixture of composition *b* is distilled, the vapour will have composition *c*, richer in the lower-boiling component. On fractional distillation, the vapour will contain progressively more tetrachloromethane until it reaches the azeotropic mixture (*a*), after which there will be no further change in composition. Starting from a composition *d* on the other side of the diagram, the vapour will have composition *e* and is now richer in the *higher-boiling* component, and fractional distillation will again yield the azeotropic mixture. From such a system, therefore, fractionation can only produce the azeotropic mixture, no matter what mixture is distilled. Complete separation of the two components is impossible.

In some mixtures, the molecules of one liquid have strong attraction for the molecules of the other liquid, usually by hydrogen bonding or compound formation. In that case the vapour pressures are lower than expected from Raoult's law, and there may be a maximum boiling point. This again gives an azeotropic mixture. Such systems are uncommon; one example is hydrogen chloride and water.

10.4. Distillation under reduced pressure

It is sometimes undesirable to distil a liquid at its normal boiling point because it decomposes at this temperature: this applies particularly to organic compounds. Reference to the vapour pressure curve of a liquid (Fig. 34) will show that the boiling point can be lowered by reducing the pressure. Distillation under reduced pressure (often called, rather loosely, vacuum distillation) is carried out by lowering the pressure inside the distilling apparatus. A water pump will serve for pressures down to about 2 kPa; below this a rotary oil pump must be used. The extent to which the boiling point can be lowered is illustrated by the following figures for phenylamine:

Pressure (kPa)	101.3	27.2	12.9	6.1	2.4	0.8
Boiling point (°C)	184	140	120	100	80	60

When a liquid is distilled in this way, it is important that both the temperature and pressure are recorded in order to assess the purity. The pressure can be measured on a mercury manometer connected to the apparatus.

10.5. Steam distillation

When two liquids are only partially miscible, there will be two separate phases present, each exerting its own vapour pressure. To simplify the problem, let us suppose that we are dealing with two liquids, A and B, which are completely immiscible: the system will then consist of two pure liquids as separate phases. The total vapour pressure p will be the sum of the individual vapour pressures of the two liquids

$$p = p_A + p_B$$

and the mixture will boil when p reaches a value equal to the atmospheric pressure. The mixture will therefore boil at a temperature lower than the boiling point of either A or B (this is because both p_A and p_B must obviously be less than atmospheric). Also, since the vapour pressure of a liquid does not depend on the amount of liquid present, p_A and p_B will not alter with the relative amounts of A and B, so that any mixture of A and B will boil at the same temperature.

The relative amounts of A and B in the vapour will depend on their respective vapour pressures. As the boiling point is constant, p_A and p_B do not alter and the vapour therefore has a constant composition. The proportions of A and B in the vapour, and therefore in the distillate, can be found by applying the ideal gas equation

$$pV = nRT$$

to the vapour (assuming that the latter is an ideal gas). If the mass of A in a volume of vapour V is m_A g, and the relative molecular mass is M_A , then

$$p_A V = \frac{m_A}{M_A} RT$$

where T is the boiling point in kelvin. Similarly, for B:

$$p_B V = \frac{m_B}{M_B} RT$$

Hence, by division,

$$\frac{p_A}{p_B} = \frac{m_A M_B}{m_B M_A}$$

$$\frac{m_A}{m_B} = \frac{p_A M_A}{p_B M_B}$$

The proportion of either liquid in the distillate is therefore governed by (a) its vapour pressure at the boiling point of the mixture, and (b) its relative molecular mass.

The most important application of this type of distillation is in the process of *steam distillation*, where one of the liquids is water and the other is a substance that is almost immiscible with water. There are many advantages to be gained by steam distillation, particularly when it is desired to separate an organic compound from an aqueous mixture containing non-volatile substances (*e.g.* salts). If the substance is not very soluble in water, and has a high relative molecular mass and an appreciable vapour pressure at about 100°C , it can be readily removed by this means. Furthermore, the temperature of distillation may be much less than the normal boiling point of the substance, with a consequently reduced danger of decomposition.

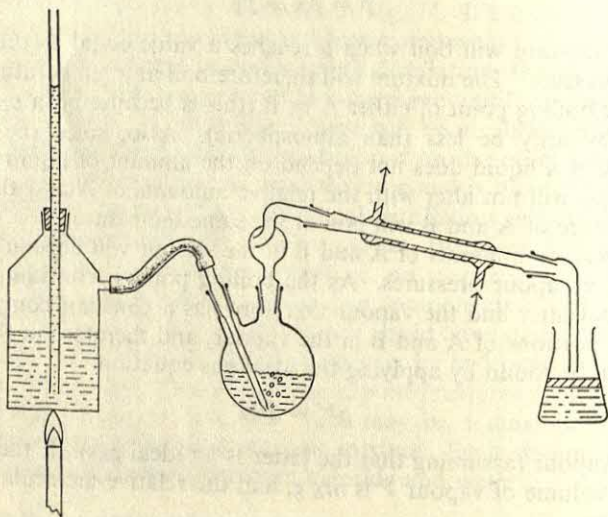


Fig. 75. Apparatus for steam distillation

An example is the separation of phenylamine from the mixture obtained after the reduction of nitrobenzene with tin and hydrochloric acid in the laboratory, or after reduction with iron and dilute hydrochloric acid as carried out industrially. The apparatus for steam distillation is shown in Fig. 75. Steam is blown through the mixture, and this serves both to keep the mixture boiling and to replace the water carried over in the distillate. Aniline is slightly soluble in water, but if this is ignored the composition of the distillate is given by:

$$\frac{\text{Mass of phenylamine}}{\text{Mass of water}} = \frac{p_{\text{phenylamine}} M_{\text{phenylamine}}}{p_{\text{water}} M_{\text{water}}}$$

The mixture is found to boil at 98.4°C (compare this with the normal boiling point of phenylamine at 184°C). At this temperature the vapour pressure of water is 95.7 kPa and, since the total pressure is 101.3 kPa , the vapour pressure of the phenylamine must be $101.3 - 95.7 = 5.6\text{ kPa}$. Inserting these figures, and the relative molecular masses, in the above equation:

$$\frac{\text{Mass of phenylamine}}{\text{Mass of water}} = \frac{5.6 \times 93}{95.7 \times 18} = 0.302$$

The percentage of phenylamine in the distillate is therefore $100 \times 0.302/1.302 = 23.2\%$. This composition will, in theory, remain constant until all the phenylamine has been distilled over. In practice, owing to the slight solubility of phenylamine in water there will still be some left in solution when the separate phenylamine phase has been distilled off.

Although the boiling point of the mixture and the composition of the distillate both depend on the total pressure, there is little variation over the normal range of atmospheric pressure. It is therefore unnecessary to measure either the barometric pressure or the temperature of distillation.

QUESTIONS

G.C.E.

1. (a) Mixtures of water and methanol obey Raoult's vapour pressure law. (i) State Raoult's Law. (ii) If the vapour pressure of pure water at 298 K is 3.2 kN m^{-2} , calculate the partial vapour pressure of water in a mixture of 36 g water and 32 g methanol at this temperature. ($H = 1, C = 12, O = 16$.)

(b) Propan-1-ol and propan-2-ol have boiling points of 97°C and 82°C respectively, and a mixture of the two alcohols behaves ideally. (i) Explain the difference in boiling points of the two alcohols. (ii) On graph paper sketch the composition-temperature curves (liquid and vapour) for mixtures of the two alcohols. (iii) What is the approximate boiling point of a mixture of the two alcohols in which the mole fraction of propan-1-ol is 0.2 ?

(c) Mixtures of ethanol (b.p. 78°C) and ethyl ethanoate (b.p. 77°C) show positive deviations from Raoult's Law. Would you expect the temperature of ethanol to increase or decrease on adding ethyl ethanoate? Explain your answer. [London]

2. Ethanol (b.p. 78.5°C) and water form a constant boiling mixture having a boiling point of 78.2°C and a composition of 95.6% ethanol. (a) Define the term *constant boiling mixture*. (b) Sketch, and label fully, the boiling point/composition diagram for ethanol and water. (c) An ethanol/water mixture shows positive deviations from Raoult's Law. Explain and account for this and state the law. (d) What intermolecular change takes place when ethanol

is added to water? (e) State qualitatively the result of distilling (i) a mixture containing 75% ethanol, (ii) a mixture containing 97.5% ethanol. (f) State with reasons which one of the following pairs of substances most closely obeys Raoult's Law: (i) $\text{C}_2\text{H}_5\text{NH}_2$ and $\text{C}_6\text{H}_5\text{NH}_2$, (ii) CH_3COCH_3 and $\text{CH}_3\text{COC}_2\text{H}_5$, (iii) C_6H_6 and $\text{C}_6\text{H}_5\text{CH}_3$. [A.E.B., 1976]

3. (a) What is meant by (i) *saturated vapour pressure*, (ii) *partial pressure*?

(b) Explain the process of steam distillation, and state why it is used in the preparation of phenylamine (aniline) from nitrobenzene.

(c) The vapour pressures of pure water and pure phenylamine (aniline) at the stated temperatures are:

Temperature in °C	85	90	95	100	105
Vapour pressure of water in kPa	57.9	70.1	84.5	101.3	120.5
Vapour pressure of phenylamine in kPa	3.0	3.9	4.9	6.1	7.3

With the aid of suitable graphs (i) find to the nearest °C the temperature at which a mixture of phenylamine (aniline) and water will steam distil under standard atmospheric pressure. (ii) Calculate the percentage by mass of phenylamine (aniline) which would be expected to be present in the distillate.

[A.E.B., 1978]

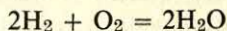
CHAPTER 11

THERMOCHEMISTRY AND THERMODYNAMICS

11.1. Energy changes in chemical reactions

When a chemical reaction takes place, energy in various forms may be either emitted or absorbed. For example, during many reactions the temperature tends to rise, showing that heat is being evolved; in other cases a fall in temperature indicates an absorption of heat. When a chemical reaction takes place in an electrical cell, such as the lead-acid accumulator, electrical energy is produced. A knowledge of the amount of energy produced by a particular reaction is often of direct practical importance; for example, it is necessary to know how much heat a certain weight of fuel will give out when it is burnt. This is one of the reasons why *thermochemistry*—the study of heat changes in chemical reactions—is an important subject.

Consider the combination of hydrogen and oxygen to form water:



During this reaction, heat is given out, and the amount of heat produced by the combination of a definite quantity of hydrogen and oxygen at any particular temperature is always found to be the same: it is a characteristic property of the reaction, and is evidently related to the chemical change that has taken place. Now, it is an established experimental fact that whenever a certain quantity of one form of energy is produced, an exactly equivalent quantity of another form of energy must have disappeared. This was first discovered by Joule (about 1850) when studying the conversion of mechanical energy into heat. In the above reaction, the heat given out must be accompanied by a corresponding decrease in the energy of the reacting system, in other words the molecules of water present at the end of the reaction must possess less energy than the molecules of hydrogen and oxygen that were there at the start. Here we are dealing mainly with *chemical energy*, which is the energy stored in the chemical bonds of the molecules.

Whenever energy in one form changes into another form, the fundamental assumption is made that the *total* amount of energy remains constant. This can be stated in the form of the *law of conservation of energy*: *energy can neither be created nor destroyed, but may be converted from one form into an equivalent amount of another form*. The study of energy changes in general (a subject known as *thermodynamics*) is based on general laws which have been found, by experiment, to be true for all types of system, both chemical and physical. The law of conserva-

tion of energy is one of these, and is more often known as the *first law of thermodynamics*. The justification for this law is that no exception to it has ever been found.*

For the purpose of studying heat changes in chemical reactions, the various energy changes can be summarised as follows:

(a) *The change in internal energy.* The *internal* (or *intrinsic*) energy is the total energy of the molecules. This consists partly of chemical energy, which depends on the chemical structure of the molecule, *i.e.* the numbers and types of chemical bonds; and partly of mechanical energy, *i.e.* kinetic energy of motion, rotational energy and vibrational energy. Of all these, the chemical energy is usually much the largest. We do not need to know the actual values for the internal energy, since we are always dealing with energy changes. Thus if the total internal energy of the products of a reaction is U_B , and that of the reactants is U_A , then the increase in internal energy during the reaction $A \rightarrow B$ is

$$\Delta U = U_B - U_A$$

and it is only the change in energy (ΔU) with which we are concerned.

(b) *The quantity of heat emitted or absorbed.* The majority of chemical reactions are *exothermic*, *i.e.* heat is given out (Latin *ex*, "out of"). When heat is absorbed, the reaction is *endothermic* (Greek *endon*, "within").

(c) *Mechanical energy* due to expansion or contraction of the reacting system. When a reaction takes place at a constant pressure, there will usually be a change in volume. If, for example, the volume increases, work is done, owing to the expansion against the external pressure. This represents a transfer of energy from the reacting system to its surroundings.

The unit of energy is the joule (J), which is derived from the basic SI units (*see* p. 300). The energy changes in chemical reactions are nearly always many thousands of joules when molar quantities are used, and the kilojoule (kJ) is commonly used. Thermochemical calculations often involve the combination of different energy quantities, and it is important to make sure that all quantities are in the same units, *i.e.* either all in kJ or all in J.

Some reference works still give figures in kilocalories (kcal). The conversion factor is $1 \text{ kcal} = 4.184 \text{ kJ}$.

* The laws of conservation of energy and conservation of mass are valid for chemical reactions but not for nuclear reactions, where an appreciable change in mass may occur. In this case the disappearance of a certain mass is balanced by the production of an equivalent amount of energy in accordance with the Einstein equation $E = mc^2$ (p. 11). The total of (mass + energy) remains constant, showing that mass can also be regarded as a form of energy.

11.2. Heat changes at constant pressure and at constant volume

Reactions involving liquids or solids, or between substances in solution, are normally carried out in vessels open to the atmosphere, so that the pressure remains constant during the reaction. A gaseous reaction, on the other hand, is usually contained in a closed vessel so that the volume is constant: if the same reaction were carried out at constant pressure, the energy changes could be different because of the work done in any expansion (or contraction) that might take place. Fig. 76 shows the various energy changes in both cases. When the pressure is

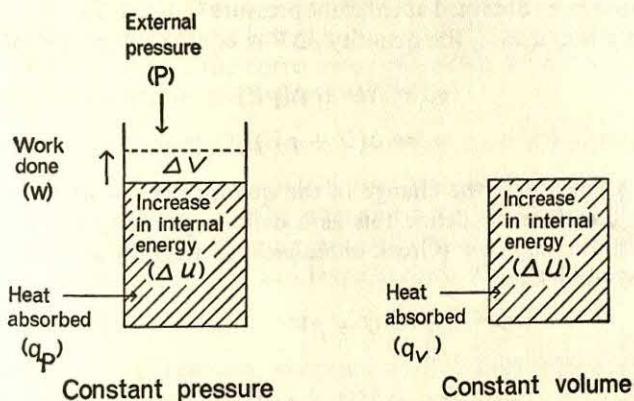


Fig. 76. Energy changes in reactions taking place at constant pressure and at constant volume

constant, it is supposed that the volume increases by ΔV , resulting in an amount of work w being done against the external pressure p . The internal energy has increased by an amount ΔU as a result of the reaction, so that a total energy of $(\Delta U + w)$ has been used up. If the system was thermally insulated, this energy would come from the kinetic energy of the molecules, and the temperature would fall. If, however, heat can enter from the surroundings so as to keep the temperature constant, then the quantity of heat absorbed (q_p) must be exactly equal to the energy used up, in accordance with the law of conservation of energy. Hence:

$$q_p = \Delta U + w$$

It was shown on p. 69 that the work done during an increase in volume ΔV against a pressure p is equal to $p\Delta V$, so that:

$$w = p\Delta V$$

and

$$q_p = \Delta U + p\Delta V$$

In the case of the same reaction taking place at constant volume, ΔV is zero and the heat absorbed is equal to the increase in internal energy:

$$q_v = \Delta U$$

The heat change during a reaction can therefore vary, depending on the conditions under which it is measured. As reactions are usually carried out at constant pressure, all heat measurements are expressed as the heat absorbed at constant pressure (q_p). When it is actually q_v that has been measured, this is converted to the quantity of heat that would have been obtained at constant pressure (see p. 172).

When p is constant, the quantity $p\Delta V$ is equal to $\Delta(pV)$, so that

$$\begin{aligned} q_p &= \Delta U + \Delta(pV) \\ &= \Delta(U + pV) \end{aligned}$$

so that q_p measures the change in the quantity $(U + pV)$. It is convenient, therefore, to define this as a definite property of the system, known as the *enthalpy* (Greek *enthalpo*, "to warm") and represented by the symbol H :

$$H = U + pV$$

so that

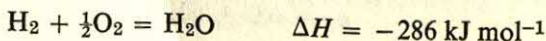
$$\begin{aligned} q_p &= \Delta(U + pV) \\ &= \Delta H \end{aligned}$$

ΔH is known as the *enthalpy change* for the reaction. It follows from the above equation that the enthalpy change for a reaction is equal to *the amount of heat absorbed when the reaction is carried out at constant pressure*. In the majority of chemical reactions heat is given out, so that both q_p and ΔH are negative; but for some reactions heat is absorbed and ΔH is positive. To sum up:

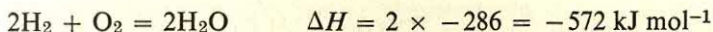
- (a) For an *exothermic* reaction (heat given out), ΔH is *negative*.
- (b) For an *endothermic* reaction (heat absorbed), ΔH is *positive*.

11.3. Enthalpy of reaction

The quantity of heat evolved or absorbed during any given reaction will depend on the actual amounts of the substances that have reacted. This is fixed by defining the *enthalpy of reaction* as *the enthalpy change (ΔH) due to reaction between the amounts of the substances, in moles, shown by the chemical equation*. Thus when hydrogen and oxygen combine at 25°C the enthalpy of reaction can be stated as follows:



This means that the combination of one mole of hydrogen with half a mole of oxygen to form one mole of water, at 25°C, results in the evolution of 286 kJ of heat. It would be just as correct to write:



In stating the ΔH value given above, the temperature was specified; this is necessary because enthalpies of reaction vary with temperature. The appropriate temperature, in kelvin, should always be given; e.g. ΔH_{298} .

The enthalpy of reaction also depends on the physical state of both the reactants and products, *i.e.* whether they are gaseous, liquid or solid. This is shown by adding the letters g (gas), l (liquid) or s (solid),* after each constituent, so that the correct way of writing the *thermochemical equation* for the reaction given above would be:



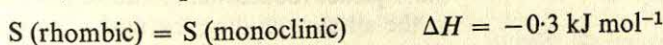
If the water had been produced in the form of water vapour, *i.e.* gaseous, the enthalpy would be altered by an amount equal to the enthalpy of vaporisation of water, which is 44 kJ mol⁻¹ at 25°C. The vaporisation of water, written as a thermochemical equation, would be:



The total enthalpy of reaction, starting from hydrogen and oxygen and finishing with water vapour, is therefore given by:



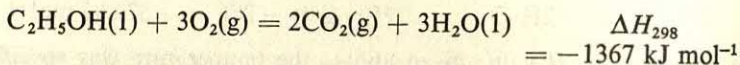
When a solid can exist in allotropic forms, the particular form involved must be stated, since there is an enthalpy change when one allotrope changes into another. When rhombic sulphur changes into the monoclinic form, for example, heat is evolved:



In the case of organic compounds, a very important reaction to study is combustion, since most compounds that contain only carbon, hydrogen and oxygen can readily be burnt to form carbon dioxide and water. The *enthalpy of combustion* is defined as *the enthalpy change (ΔH) when one mole of a compound is burnt completely in oxygen*. The definition is not restricted to organic compounds, and the enthalpies of combustion of inorganic compounds and certain elements (e.g. carbon, hydrogen, sulphur) are to be found in tables. The words "completely burnt" in the definition must be emphasised, because it is possible to burn an organic compound so as to finish with both carbon monoxide and carbon dioxide. To avoid this uncertainty, the combustion is always carried out with a large excess of oxygen present, and it is

* Solids may also be indicated by c (standing for crystal).

assumed that the products are *only* carbon dioxide and water. Thus the information that the enthalpy of combustion of ethanol is $\Delta H = -1367 \text{ kJ mol}^{-1}$ at 25°C can be put in the following form:



Heats of combustion are sometimes quoted simply as a positive quantity of heat, meaning the heat *evolved*. This should not cause any confusion, because combustion reactions are always exothermic and the value of ΔH is therefore always negative.

11.4. Measuring heats of reaction

Heat is a quantity that cannot be measured directly, but if a reacting system is insulated from its surroundings so that heat cannot pass between them the temperature of the system will either rise or fall, depending on whether the reaction is exothermic or endothermic. The change in temperature can be measured and from it the amount of heat can be calculated. The apparatus used for such measurements is called a *calorimeter*. Two necessary requirements for calorimetric measurements are (a) that the reaction goes to completion, so that the amount of material which has reacted is known exactly, and (b) that the reaction is fast, preferably being over within a few minutes.

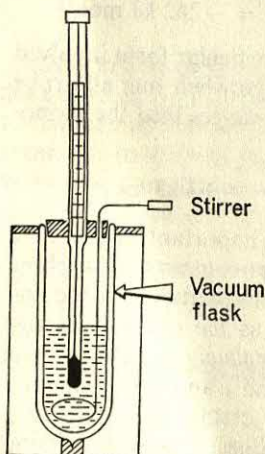


Fig. 77. Calorimeter for measuring heats of reaction in solution

For studying reactions in solution, the calorimeter consists essentially of an insulated vessel in which the reaction is carried out. An unsilvered vacuum flask may be used to provide thermal insulation (Fig. 77), while an outer jacket reduces temperature fluctuations in the air surrounding the flask. An efficient stirrer must be provided, so that the reactants are properly mixed and the temperature is kept uniform throughout the solution. For accurate work, the thermometer must be capable of reading to 0.001 degree. The reaction will probably involve mixing two solutions, or adding a solid to a solution, and it is essential that the temperature of both reactants is known accurately before the reaction starts. The best method of ensuring this is to have them both inside the calorimeter, one contained in a small separate vessel, so that they can attain the same temperature before they are mixed.

It is impossible to insulate a calorimeter completely from its surroundings, and when there is a difference in temperature between the two some heat is bound to enter or leave the calorimeter. This is the chief source of error in calorimetric measurements. Fig. 78 shows how the temperature inside a calorimeter altered during the course of an experiment. The reactants were a little below room temperature at the start, and there was a slight flow of heat into the calorimeter which caused a small but steady rise in temperature. The reaction was exothermic, and raised the temperature inside the calorimeter above that

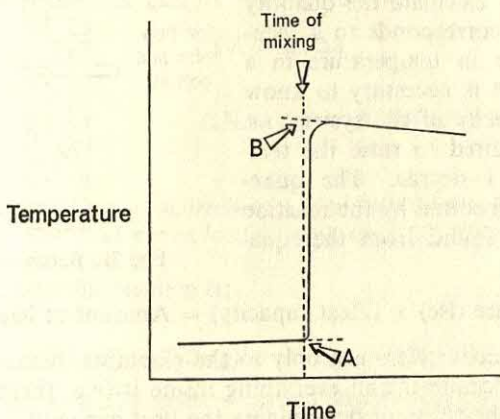


Fig. 78. Method of obtaining the corrected rise in temperature (AB)

of the surroundings; heat was then lost, and the temperature fell steadily. To find the true rise in temperature, the two straight lines obtained by plotting the temperatures before and after mixing are produced to cut a vertical line drawn at the time of mixing, giving the two points A and B on the diagram. The difference between A and B is the corrected temperature rise.

Errors due to heat losses can be eliminated by using an *adiabatic calorimeter* (Greek *a-diabatos*, "not to be crossed"). Here the calorimeter vessel is surrounded by a jacket containing water, the temperature of which is automatically kept the same as the temperature of the liquid inside the vessel. As the reacting system and its surroundings are always at the same temperature, no heat passes in either direction.

For heats of combustion, the *bomb calorimeter* (Fig. 79) is used. This consists of a strong metal vessel capable of withstanding high pressures. A weighed amount of the compound is placed in the crucible, with a wire (connected to external electrodes) for starting the reaction. The top is screwed firmly on, and the bomb is then filled with oxygen

under pressure, and placed in a container filled with water. Combustion is effected by fusing the wire, which ignites a cotton thread touching the compound, and the temperature rise of the calorimeter plus the surrounding water is measured. Corrections for heat losses are applied as before, unless the instrument is an adiabatic one.

In order to calculate the quantity of heat that corresponds to a measured change in temperature in a calorimeter, it is necessary to know the *heat capacity* of the system, *i.e.* the heat required to raise the temperature by 1 degree. The quantity of heat liberated by the reaction can then be found from the equation:

$$(\text{Temperature rise}) \times (\text{Heat capacity}) = \text{Amount of heat liberated}$$

The heat capacity refers not only to the reactants themselves, but includes the calorimeter and everything inside it (*e.g.* thermometer and stirrer). The best way of determining the heat capacity is to liberate a known amount of heat inside the calorimeter and measure the rise in temperature. This can be done after the reaction is over. In an open calorimeter a convenient way of doing it is to pass an electric current through a coil of wire immersed in the solution, the amount of heat produced being calculated from the quantity of electricity ($\text{Current} \times \text{Time}$) and the voltage between the ends of the coil. The heat capacity of a bomb calorimeter is found by burning a known weight of benzoic acid inside it, the heat of combustion of this compound being accurately known.

Measurements in an open calorimeter determine the amount of heat liberated or absorbed when known amounts of substances react at constant pressure. When this has been converted into the amount of heat that would have been *absorbed* if *molar* quantities had reacted, the figure obtained is ΔH , the enthalpy of reaction. In a bomb calorimeter, however, the volume is constant and the result obtained is ΔU , which must then be converted into the corresponding value of ΔH . The relation between the two has been shown (pp. 167, 168) to be:

$$\Delta H = \Delta U + p\Delta V$$

In calculating the increase in volume ΔV , the volume of any solids or

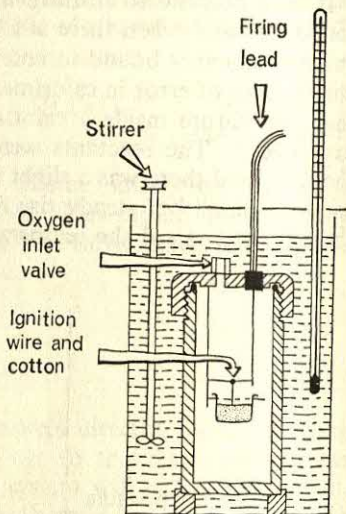


Fig. 79. Bomb calorimeter

liquids that are formed or destroyed during the reaction can be ignored: it is only gases that have to be taken into account. This is because the volume occupied by solids is so small that ΔV would be negligible. If, when the reaction takes place, the numbers of moles of gas increase by Δn , and V is the volume of one mole of gas, then:

$$\Delta V = V\Delta n$$

and

$$p\Delta V = PV\Delta n$$

and since, for 1 mole of gas, pV is equal to RT ,

$$p\Delta V = RT\Delta n$$

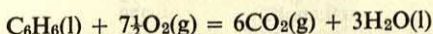
so that

$$\Delta H = \Delta U + RT\Delta n$$

EXAMPLE

When benzene is burnt completely in a bomb calorimeter, the heat evolved is equivalent to 3297.8 kJ per mole of benzene, at 25°C. What is the enthalpy of combustion of benzene?

The equation for the reaction is:



The reaction starts with $7\frac{1}{2}$ moles of gas and finishes with 6 moles, so that the increase in the numbers of moles of gas is:

$$\begin{aligned}\Delta n &= 6 - 7\frac{1}{2} \\ &= -1\frac{1}{2}\end{aligned}$$

Since the measurement was made at constant volume, the heat *absorbed* is equal to ΔU , i.e. $\Delta U = -3297.8$ kJ.

$$\begin{aligned}\Delta H &= \Delta U + RT\Delta n \\ &= -3297.8 - 8.31 \times 10^{-3} \times 298 \times 1\frac{1}{2} \\ &= -3297.8 - 3.7 \\ &= -3301.5 \text{ kJ mol}^{-1}\end{aligned}$$

11.5. Standard enthalpy of formation

In tables of thermodynamic data, it will be found that the only enthalpy figures given are for chemical compounds, and are in the form of the *standard enthalpy of formation* (ΔH_f°). The reason why only these figures are given is because it is possible to calculate the enthalpy change for any reaction, if the standard enthalpies of formation of all the compounds taking part in the reaction are known (see § 11.6). This is only possible if the enthalpy of formation represents the enthalpy change when the compound is formed *from its elements*.

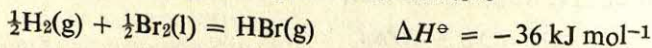
It has already been stated that enthalpies of reaction can vary both

with the states of matter of the reactants, and also with the temperature. In defining a *standard* quantity, shown by the superscript $^\circ$, these conditions are fixed by choosing a standard temperature and pressure, usually 25°C and atmospheric pressure. Under these conditions the elements are always in the same state (either solid, liquid, or gaseous). For these reasons, the standard enthalpy of formation of a compound (ΔH_f°) is defined as *the enthalpy change when one mole of the compound is formed from its elements in their normal states at 25°C (298 K) and atmospheric pressure*. The standard enthalpies of formation of some compounds are shown in Table 6.

TABLE 6. STANDARD ENTHALPIES OF FORMATION

Substance	ΔH_f° (kJ mol^{-1})
$\text{H}_2\text{O}(\text{l})$	-286
$\text{H}_2\text{O}(\text{g})$	-242
$\text{CO}(\text{g})$	-111
$\text{CO}_2(\text{g})$	-394
$\text{HCl}(\text{g})$	-92
$\text{HBr}(\text{g})$	-36
$\text{NH}_3(\text{g})$	-46
$\text{SO}_2(\text{g})$	-297
$\text{SO}_3(\text{g})$	-395
$\text{CH}_4(\text{g})$	-75
ethanol(l)	-278
benzene(l)	83

To illustrate the meaning of the definition given above, it will be seen from the table that the standard enthalpy of formation of hydrogen bromide (gaseous) is $\Delta H_f^\circ = -36 \text{ kJ mol}^{-1}$. At the standard temperature and pressure, hydrogen is a gas and bromine is a liquid; the appropriate thermochemical equation is therefore

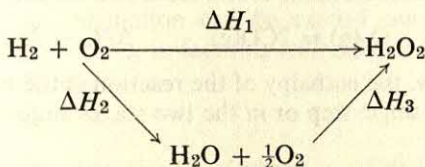


11.6. Hess's law

In many cases it is impossible to measure the enthalpy of reaction directly, and this applies particularly to enthalpies of formation. For example, it is not possible to cause hydrogen and oxygen to combine in a calorimeter to form hydrogen peroxide, so the enthalpy of formation of this compound must be found by combining heat measurements made on related reactions. This indirect method is based on *Hess's law*, which states that *the enthalpy change in a chemical reaction is the same, whether the reaction takes place directly or in a number of stages*.

The application of this law can be illustrated in the following way. The practical difficulty of determining the enthalpy of formation of hydrogen peroxide directly has already been mentioned. However, the decomposition of hydrogen peroxide into water and oxygen is a reaction

that can be studied, and so is the combination of hydrogen and oxygen to form water. The formation of hydrogen peroxide could be written either as a single step, or in two separate stages, as shown below.



In accordance with Hess's law, the enthalpy of formation of H_2O_2 (ΔH_1) is the same as the total enthalpy change when the alternative path via reactions 2 and 3 is taken, *i.e.*:

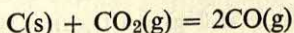
$$\Delta H_1 = \Delta H_2 + \Delta H_3$$

The enthalpy of formation of water (ΔH_2) is -286 kJ mol^{-1} . The enthalpy of decomposition of H_2O_2 is -98 kJ mol^{-1} , but this is the reverse of reaction 3: therefore, $\Delta H_3 = +98 \text{ kJ mol}^{-1}$. Hence:

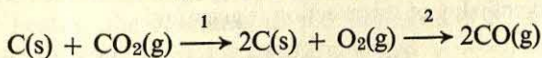
$$\begin{aligned}
 \Delta H_1 &= -286 + 98 \\
 &= -188 \text{ kJ mol}^{-1}
 \end{aligned}$$

Hess's law is a direct consequence of the first law of thermodynamics (conservation of energy). Referring to the diagram for the formation of hydrogen peroxide given above, it would be possible to convert hydrogen and oxygen into water (step 2), then convert the water and the remaining oxygen into hydrogen peroxide (step 3), and finally decompose the hydrogen peroxide (step 1 reversed) so as to finish up with hydrogen and oxygen again. If Hess's law were not obeyed, it would be possible to finish up with either more or less energy than at the start, so that energy would either have been created or destroyed. This would be contrary to the first law of thermodynamics.

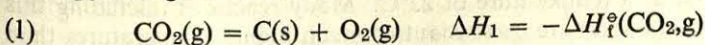
Standard enthalpies of formation can be used to calculate the enthalpy change for any reaction, by the use of Hess's law. Thus suppose that the enthalpy change for the following reaction is required:



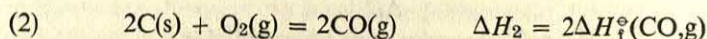
This reaction could be imagined as taking place in two separate stages:



Stage (1) involves the decomposition of one mole of CO_2 into its elements, which is the reverse of the formation reaction for CO_2 . The enthalpy change is therefore as follows:



Note that when a thermochemical reaction is reversed, the sign (but not the magnitude) of the enthalpy change is altered. The reaction in stage (2) is the formation of two moles of CO from its elements (note that the second carbon atom comes from the original reactants):

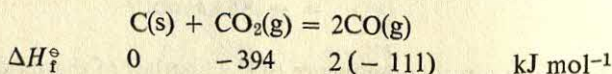


From Hess's law, the enthalpy of the reaction is the same whether it is carried out in a single step or in the two stages suggested. It therefore follows that:

$$\begin{aligned} \Delta H^\circ &= \Delta H_1 + \Delta H_2 \\ &= 2\Delta H_f^\circ(\text{CO,g}) - \Delta H_f^\circ(\text{CO}_2,\text{g}) \end{aligned}$$

This result can be stated more simply by saying that *the enthalpy change for a reaction is equal to the sum of the enthalpies of formation of the products minus the sum of the enthalpies of formation of the reactants*.

The simplest way of calculating an enthalpy change by this method is to write down the chemical equation, then add the values for the standard enthalpies of formation as obtained from tables. Thus for the above reaction:



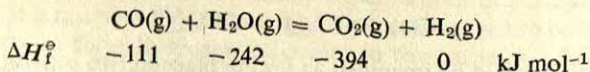
and the value of ΔH° for the reaction is then given by the difference between the totals for the products and the reactants:

$$\begin{aligned} \Delta H^\circ &= 2(-111) - (-394) \\ &= 172 \text{ kJ mol}^{-1} \end{aligned}$$

Note that the standard enthalpies of formation of elements are, by definition, zero.

EXAMPLE

In the Bosch process for the manufacture of hydrogen, carbon monoxide and steam react to give carbon dioxide and hydrogen. What is the standard enthalpy of reaction?



The standard enthalpy of this reaction is given by:

$$\begin{aligned} \Delta H^\circ &= -394 - (-111 - 242) \\ &= -41 \text{ kJ mol}^{-1} \end{aligned}$$

It should be remembered that this figure applies to the reaction when carried out at a temperature of 25°C. Many reactions (including this particular example) are carried out at much higher temperatures than

this, and the enthalpy value has to be corrected by the method described in the following section (§ 11.7).

The enthalpies of formation of organic compounds can seldom be measured directly, and many of them are calculated from enthalpies of combustion. The calculation can be carried out in exactly the same way as described above, in fact this method may be used for any thermochemical calculation.

EXAMPLE

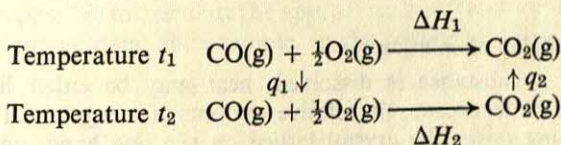
The standard enthalpy of combustion of ethanol is $-1368 \text{ kJ mol}^{-1}$: what is the standard enthalpy of formation of ethanol?

Here the enthalpy change of the reaction is known, and it is ΔH_f° for ethanol that is the unknown quantity.

$$\begin{array}{rcll}
 \text{C}_2\text{H}_5\text{OH(l)} + 3\text{O}_2\text{(g)} & = & 2\text{CO}_2\text{(g)} + 3\text{H}_2\text{O(l)} & \\
 \Delta H_f^\circ & & 0 & 2(-394) \quad 3(-286) \quad \text{kJ mol}^{-1} \\
 \Delta H^\circ \text{ (combustion)} & = & 2(-394) + 3(-286) - \Delta H_f^\circ & \\
 -1368 & = & -788 - 858 - \Delta H_f^\circ & \\
 \Delta H_f^\circ & = & 1368 - 1646 & \\
 & = & -278 \text{ kJ mol}^{-1} &
 \end{array}$$

11.7. The variation of enthalpies of reaction with temperature

Enthalpies of reaction vary somewhat with temperature. The reason for this can be seen from the following illustration, which shows the same reaction taking place at two different temperatures t_1 and t_2 , the enthalpy of reaction being ΔH_1 and ΔH_2 respectively.



There are two alternative paths by which carbon monoxide and oxygen at temperature t_1 can be transformed into carbon dioxide, also at this temperature:

- By direct reaction at temperature t_1 .
- By heating the reactants to the temperature t_2 , allowing the reaction to proceed at that temperature, and cooling the products down to t_1 after the reaction is complete.

According to Hess's law, the total enthalpy change must be the same in both cases, so that

$$\Delta H_1 = q_1 + \Delta H_2 + q_2$$

where q_1 and q_2 are the amounts of heat absorbed during the heating of the reactants and the cooling of the products respectively: these amounts can be calculated from the heat capacities, using C_p values because enthalpies of reaction refer to constant pressure conditions.

$$q_1 = [C_p(\text{CO}) + \frac{1}{2}C_p(\text{O}_2)](t_2 - t_1)$$

$$q_2 = -[C_p(\text{CO}_2)](t_2 - t_1)$$

q_2 has a negative value since heat is evolved during cooling. Substituting these values in the previous equation,

$$\begin{aligned}\Delta H_2 - \Delta H_1 &= [C_p(\text{CO}_2) - C_p(\text{CO}) - \frac{1}{2}C_p(\text{O}_2)](t_2 - t_1) \\ &= \Delta C_p(t_2 - t_1)\end{aligned}$$

where ΔC_p is equal to the heat capacity of the products minus the heat capacity of the reactants. This relationship is known as the *Kirchhoff equation*. As heat capacities also vary with temperature, it is best to use the values appropriate to the mean of the two temperatures.

EXAMPLE

In a previous example, it was found that ΔH for the reaction $\text{CO(g)} + \text{H}_2\text{O(g)} = \text{CO}_2\text{(g)} + \text{H}_2\text{(g)}$ was -41 kJ mol^{-1} at 298 K. If the reaction is carried out at 723 K, what will be the heat of reaction? (The mean values of the molar heat capacities are: CO, 30; H₂O, 36; CO₂, 45; H₂, 29 J K⁻¹ mol⁻¹.)

$$\Delta C_p = (45 + 29) - (30 + 36)$$

$$= 8 \text{ J K}^{-1} \text{ mol}^{-1}$$

$$\Delta H_{723} - \Delta H_{298} = 8(450 - 25)$$

$$\Delta H_{723} = -41\,000 + 3400$$

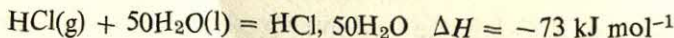
$$= -37\,600 \text{ J mol}^{-1}$$

$$= -38 \text{ kJ mol}^{-1}$$

11.8. Enthalpy of solution

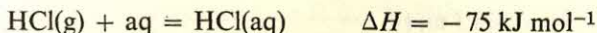
When a substance is dissolved, heat may be either liberated or absorbed; it depends on the relative amounts of energy which are used up in breaking down the crystal lattice on the one hand, and liberated during the hydration of the solute on the other (see § 8.2). The quantity of heat involved is not constant, but varies with the concentration of the final solution. This may be due to a number of factors, e.g. variation in the extent of hydration of the solute, and in some cases in the degree of dissociation.

The *enthalpy of solution* has therefore to be defined as the *enthalpy change when one mole of the solute is dissolved in a specified amount of solvent*. This can be indicated as follows:



which means that when 1 mole of HCl is dissolved in 50 moles of water, 73 kJ of heat are evolved. If the final solution is very dilute (i.e.,

such that further dilution would cause no additional heat change) the equation is written:

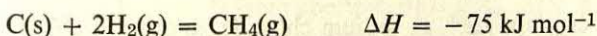


where aq represents a large volume of water.

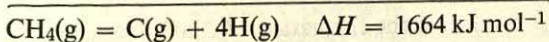
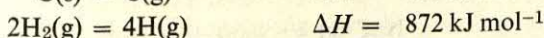
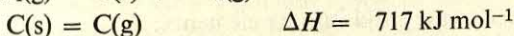
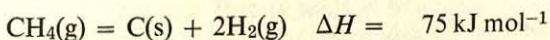
11.9. Bond energies from thermochemical data

In § 3.5 the term *bond dissociation energy* was defined as the energy required to break a chemical bond, and a list of values was given in Table 2. We shall now see how bond dissociation energies can be calculated from thermochemical data.

The enthalpy of formation of methane is given by the equation:

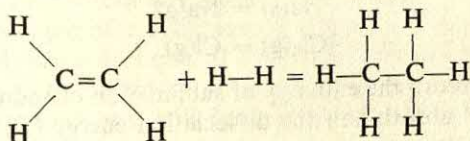


If we can measure the heat absorbed when one mole of methane is split up into separate atoms of carbon and hydrogen, this will give the energy of four C—H bonds. This can be done by reversing the above equation, and combining it with the enthalpy of sublimation of carbon and the energy required to dissociate the hydrogen molecule (the latter can be obtained from spectral measurements).



The C—H bond energy is therefore $1664/4 = 416 \text{ kJ mol}^{-1}$.

It is often possible to calculate the approximate enthalpy of a reaction from bond energy data: for example, in the hydrogenation of ethene



it can be imagined that first of all the ethene and hydrogen are dissociated into atoms, which will absorb energy equivalent to the four C—H bonds, one C=C bond, and one H—H bond that have to be broken. If the ethane molecule is then formed from the separate atoms, the C—C bond energy, plus six times the C—H bond energy, will be evolved. The enthalpy of reaction is the overall amount of energy absorbed, and is therefore given by:

$$\begin{aligned} \Delta H &= 4(\text{C}-\text{H}) + (\text{C}=\text{C}) + (\text{H}-\text{H}) - 6(\text{C}-\text{H}) - (\text{C}-\text{C}) \\ &= (\text{C}=\text{C}) + (\text{H}-\text{H}) - 2(\text{C}-\text{H}) - (\text{C}-\text{C}) \end{aligned}$$

Using bond energy values from Table 2:

$$\begin{aligned}\Delta H &= 611 + 436 - 2 \times 413 - 347 \\ &= -126 \text{ kJ mol}^{-1}\end{aligned}$$

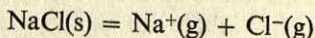
(The experimental value is -137 .)

11.10. Lattice energy: the Born-Haber cycle

The enthalpy of formation of a solid is, by definition, the quantity of heat absorbed when 1 mole of the solid is formed from its elements in their normal states, *e.g.* for sodium chloride:

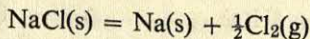


For ionic crystals, such as sodium chloride, another useful quantity is the *lattice energy* (U): this is defined as the energy required to separate the ions in the crystal until they are far apart, in other words, to convert the solid into gaseous ions:



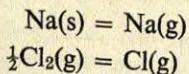
The same result could be achieved in a number of separate steps, as follows:

(a) Convert the solid into its elements:



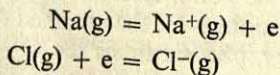
This is the reverse of the formation of NaCl from its elements, so that the heat absorbed is $-\Delta H_f$.

(b) Convert both elements into gaseous atoms:



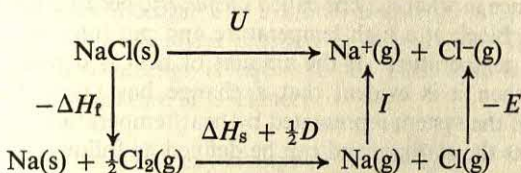
The first will absorb the enthalpy of sublimation of sodium (ΔH_s), and the second will absorb half the dissociation energy (D) for 1 mole of chlorine molecules.

(c) Ionise the sodium and chlorine atoms:



The energy absorbed in the first process is known as the *ionisation energy* (I). The formation of a negative ion involves the *electron affinity* (E), which is the energy *liberated* when one mole of ions is formed; the second process therefore *absorbs* an energy of $-E$.

The various steps can be written in the form of a *Born-Haber cycle*:



By applying Hess's law it will be seen that:

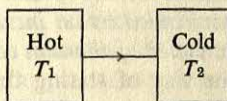
$$U = -\Delta H_f + \Delta H_s + \frac{1}{2}D + I - E$$

Of the quantities on the right-hand side of the equation, all except E can be measured experimentally. ΔH_f is found from thermochemical measurements, and I and D from spectroscopic data. It is possible to calculate E , and hence the lattice energy U can be found. It is also possible to calculate U , assuming that the crystal is purely ionic, and the equation can then be used either to find the electron affinity E or to detect any covalent character in the crystal bonding.

11.11. Spontaneous processes and free energy

This section might have been entitled "How can you tell whether a reaction will occur?" because that is what it is about. It is easy to write a chemical equation to show a possible reaction, but this does not mean that it will actually take place. One way of finding out is to try it experimentally, but it would obviously be better if the result could be predicted without having to do the experiment. If we approach this problem from the point of view of energy changes, then there is no need to confine our attention to chemical reactions, because the general laws governing such changes apply to all systems, whether physical or chemical. What we wish to know is what makes a change take place *spontaneously*, i.e. without any outside intervention.

A simple example of a spontaneous change is the passage of heat from a hot body to a colder one. If a hot block of metal at a temperature T_1 is connected, by means of a copper rod, to a colder block at a temperature T_2 , then heat will flow spontaneously from hot to cold.



Suppose a small amount of heat q is allowed to pass, too small to cause any appreciable change in the temperature of the blocks. What we now wish to discover is whether the system has altered in any way as a result of the spontaneous change that has occurred. The total energy of the system has not altered, since all that happened is that the same quantity of energy q has been transferred from one block to the other.

However, although there is no difference in the *quantity* of heat, there is a difference in what may be called its *quality*, because it was taken out of the first block at a high temperature and put into the second block at a lower temperature. If the amount of heat is divided by the temperature, then it is evident that a change has taken place in some property of the system represented by heat/temperature. This property is known as the *entropy*, and can be defined as follows:

$$\text{Increase in entropy} = \frac{\text{Quantity of heat absorbed}}{\text{Temperature (kelvin)}}$$

The entropy changes in the hot and cold blocks can now be worked out:

$$\text{Increase in entropy of hot block} = \frac{-q}{T_1}$$

$$\text{Increase in entropy of cold block} = \frac{+q}{T_2}$$

$$\text{Total increase in entropy} = \frac{q}{T_2} - \frac{q}{T_1}$$

Since T_2 is less than T_1 , this means that the total entropy of the system has increased as a result of the spontaneous change.

It is now necessary to find out what happens when no spontaneous change can occur, *i.e.* when the system is in a state of equilibrium. This will be the case when both metal blocks are at the same temperature, for if they are then connected, no heat will flow between them. If we imagine a condition very close to equilibrium, *i.e.* T_2 is very slightly less than T_1 , then heat will flow slowly from left to right. Since T_1 is almost exactly the same as T_2 , the entropy changes will be:

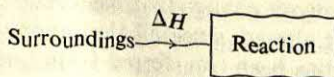
$$\text{Increase in entropy of left-hand block} = \frac{-q}{T_2}$$

$$\text{Increase in entropy of right-hand block} = \frac{+q}{T_2}$$

$$\text{Total increase in entropy} = \frac{q}{T_2} - \frac{q}{T_2} = 0$$

The two conclusions arrived at above can be stated as follows: *a spontaneous change is accompanied by an increase in the total entropy, but for a change carried out under equilibrium conditions the entropy does not alter.* This is also one way of stating the *second law of thermodynamics*.

When this law is applied to chemical reactions, it must be remembered that a certain quantity of heat (the heat of reaction) is exchanged between the reacting system and the surroundings. The *total* entropy



change therefore includes the entropy changes of both the reacting system and the surroundings. The symbol for entropy is S , so that the entropy change for a chemical reaction is written ΔS . The entropy change of the surroundings is equal to the heat absorbed ($-\Delta H$) divided by the temperature (T). Hence:

$$\text{Total entropy change} = \Delta S - \frac{\Delta H}{T}$$

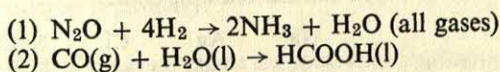
A chemical reaction will therefore occur spontaneously if this quantity is positive, and will be at equilibrium if it is zero. In practice, it is found convenient to define a new function, called the *free energy* (G), so that the free energy change for a reaction (ΔG) is given by

$$\Delta G = \Delta H - T\Delta S$$

Comparison of this equation with the conditions stated above will show that ΔG is negative for a spontaneous reaction, and zero for a reaction that is at equilibrium.

Several methods are available for measuring free energy changes: in one of these, both the enthalpy change (ΔH) and the entropy change for the reaction (ΔS) are determined, and ΔG is calculated from the equation given above. Since ΔG varies with temperature, values must always refer to a stated temperature. Free energy changes can be combined, in accordance with Hess's law, in exactly the same way as enthalpies of reaction (§ 11.6). This makes it possible to tabulate free energies of formation of compounds (from their elements), and to work out ΔG for a reaction from these figures: the method is again exactly the same as the use of enthalpies of formation.

As an example of the application of free energies, let us consider the feasibility of the following reactions:



ΔG for reaction (1) is found to be -366 kJ mol^{-1} : this reaction therefore takes place spontaneously and is a possible one. For reaction (2) $\Delta G = +29 \text{ kJ mol}^{-1}$, and this reaction is of no practical use (the positive value actually means that reaction will occur spontaneously in the reverse direction). These values of ΔG , however, refer to a temperature of 25°C and atmospheric pressures. It is quite possible that under different conditions (*e.g.* high temperature, increased pressure) a positive value of ΔG may change to a negative one, thus making the reaction possible.

Another very important practical consideration is that although a reaction may be thermodynamically *possible*, it may be so slow as to be of no practical use unless it can be speeded up by using a higher temperature or a catalyst.

QUESTIONS

G.C.E.

1. (a) (i) Define enthalpy of formation ΔH_f° of a compound. (ii) What extra conditions must be imposed to specify the standard enthalpy of formation ΔH_f° of a compound?

(b) When ethanol burns in oxygen, carbon dioxide and water are formed.

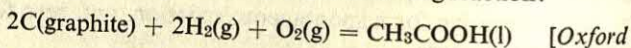
(i) Write the equation which describes this reaction. (ii) Using the data

ΔH_f° for ethanol (l)	= -277.0 kJ mol ⁻¹
ΔH_f° for carbon dioxide (g)	= -393.7 kJ mol ⁻¹
ΔH_f° for water (l)	= -285.9 kJ mol ⁻¹

calculate the value of ΔH° for the combustion of ethanol.

[J.M.B.]

2. Without giving experimental detail, indicate what experiments would have to be performed, and how the results obtained would be used, to determine the enthalpy change (ΔH) at 298 K for the following reaction:



3. State the first law of thermodynamics in terms of heat and work, defining these quantities carefully.

Why is enthalpy more useful than internal energy in discussing heat changes accompanying chemical reactions? What is the relationship between these two quantities?

From the bond enthalpies of C—C, C=C, and the enthalpies of atomisation of carbon and hydrogen (pp. 179 and 42), calculate the standard enthalpy of formation of ethane and ethene. Why cannot the standard enthalpy of formation of benzene be determined from these data?

[O. and C.]

4. Describe the lattice structure of (a) copper, (b) graphite, and show how they can be used to explain two characteristic physical properties of each of these substances.

Calculate the lattice energy of (i) sodium chloride, (ii) silver chloride, using a suitable thermochemical cycle and the following data:

	Na	Ag	Cl	NaCl	AgCl
Enthalpy of atomisation/ kJ (mol of atoms) ⁻¹	+108	+286	+121		
First ionisation energy/ kJ mol ⁻¹	+494	+732			
Electron affinity/kJ mol ⁻¹			-364		
Enthalpy of formation/ kJ mol ⁻¹				-411	-127

Comment on your answers in (i) and (ii) in relation to the values of -770 kJ mol⁻¹ and -700 kJ mol⁻¹ respectively, obtained by calculation on the basis of the electrostatic forces of attraction between the oppositely charged ions in the lattice.

[Cambridge]

CHAPTER 12

CHEMICAL KINETICS

12.1. The factors affecting the rate of a chemical reaction

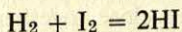
One of the most important pieces of information about a chemical reaction is the speed at which it will take place. If a certain reaction is to be usefully employed, it is necessary to know the conditions under which it will proceed at a reasonable rate. Thus it is known that hydrogen and oxygen will react to form water, but if the two gases are mixed at ordinary temperatures nothing appears to happen because the reaction is extremely slow. If, however, the temperature is raised a few hundred degrees, the reaction may occur with explosive violence.

Different reactions vary widely in velocity. At room temperature some reactions are very fast, for example ionic reactions in solution often take place practically instantaneously. Some reactions, on the other hand, are so slow that it is not possible to detect any change at all. Between these two extremes are many reactions which take place at measurable speed, so that it may take some time to obtain a good yield of the products; this is often the case, for example, in organic preparations.

If a reaction is slow under a certain set of conditions, it does not follow that it is useless, for the rate of a reaction can be profoundly affected by the following factors: the concentration of the reactants, the temperature, and the presence of a catalyst. These various factors will be considered separately.

12.2. The effect of concentration: the reaction rate law

It was discovered around 1850 that *the rate of a reaction is proportional to the concentrations of the reacting substances*. This is the *reaction rate law*. For example, when hydrogen and iodine (both in the gaseous state) are heated together, they combine to form hydrogen iodide in accordance with the equation

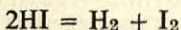


and the rate of reaction is proportional to the concentrations of both hydrogen and iodine:

$$\text{Rate} = k[\text{H}_2][\text{I}_2]$$

The proportionality constant k is known as the *rate constant* of the reaction. The square brackets represent concentrations in mol dm^{-3} .

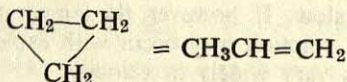
This is an example of a *bimolecular reaction*, because there are two molecules taking part. The reverse of this reaction, *i.e.* the decomposition of hydrogen iodide:



involves a reaction between two molecules of HI and so is also bimolecular. The rate, as before, is proportional to the concentrations of both reacting molecules:

$$\begin{aligned}\text{Rate} &= k[\text{HI}][\text{HI}] \\ &= k[\text{HI}]^2\end{aligned}$$

When molecules react singly, which they can do by either decomposing or undergoing molecular rearrangement, the reaction is *unimolecular*. When cyclopropane is heated, it is converted into propene:



and the rate is proportional to the concentration of cyclopropane.

It must not be assumed from this that the relation between the velocity of any reaction and the concentrations of the reactants can be deduced simply by inspecting the chemical equation, because most chemical reactions are complex, that is, they take place in a number of separate steps. The equation merely states how many molecules of the reactants are used up and what are the final products; it gives no information about the mechanism of the reaction. The examples given so far have all been simple reactions that proceed in a single step as shown by the equation. There is no way of telling whether a reaction is simple or complex except by studying its kinetics, *i.e.* the way in which the rate depends on the concentrations of the reactants and on certain other factors. This is a very important application of the study of reaction rates.

To understand why reactions obey the rate law, let us consider the gaseous reaction between hydrogen and iodine mentioned above. The mixture will consist of hydrogen and iodine molecules moving at high speed and continually colliding with one another. Before a reaction can take place, a hydrogen molecule must collide with an iodine molecule, and while the two are close together there will have to be rearrangement of the chemical bonds so that two molecules of hydrogen iodide are formed. It is reasonable to suppose that the rate at which this takes place will depend on the frequency with which hydrogen and iodine molecules collide. Consider a single iodine molecule: the rate at which it will collide with hydrogen molecules will be proportional to the concentration of the latter, which is also proportional to $[\text{H}_2]$. The number of iodine molecules is also proportional to $[\text{I}_2]$, so that:

Rate of collision between *one* I_2 molecule and all H_2 molecules $\propto [H_2]$

Rate of collision between *all* I_2 molecules and all H_2 molecules
 $\propto [H_2][I_2]$

Assuming that the reaction proceeds at a speed proportional to the rate of collision,

$$\text{Reaction rate} \propto [H_2][I_2]$$

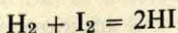
which is the reaction rate law.

The actual collision rate can be calculated from the kinetic theory of gases. For hydrogen and iodine at 300°C , both at 0.01 mol dm^{-3} concentration, the calculation gives 1.6×10^{31} collisions per second in a volume of 1 dm^3 . The actual velocity of this reaction, however, when measured experimentally at this temperature, shows that the numbers of pairs of molecules reacting per second is only 1.5×10^{16} . It therefore appears that only one in every 10^{15} collisions is successful in causing a reaction to take place. The reason why only this minute fraction of the total number of collisions results in chemical reaction will be explained in the next section.

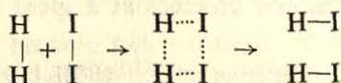
12.3. The effect of temperature on reaction rates

It is a matter of common experience that reactions are speeded up if they are heated. In nearly every case, *the rate of a chemical reaction increases as the temperature is raised*. Consequently, reactions are often carried out at elevated temperatures so that a good yield of the products can be obtained in a reasonable time. In the laboratory, examples of this include hydrolyses and other organic reactions, the reaction mixture being heated up to the boiling point; industrially, far higher temperatures may be used, with the reactants under pressure or in the gaseous state. In most cases, the velocity of a reaction increases very rapidly with temperature: for example, in the decomposition of dinitrogen pentoxide the time taken for half the original amount of material to decompose is 12 minutes at 50°C , 5 hours at 25°C and 10 days at 0°C .

If we apply Le Chatelier's principle, an increase in temperature will cause the reaction to alter so as to oppose the change, which it can only do by absorbing heat (*i.e.* energy). Since it does this by increasing in velocity—in other words, more reaction is taking place in a given time—it follows that energy is always absorbed when a reaction takes place. At first sight this might appear to contradict the fact that the overall heat of reaction may be either positive or negative, *i.e.* heat is either evolved or absorbed. The difficulty was overcome by a theory put forward by Arrhenius, which is best explained by reference to an actual example. In the reaction in which hydrogen and iodine react to form hydrogen iodide, the overall result is given by the equation



but it is now known that this can only take place if, when a molecule of hydrogen and a molecule of iodine collide, an unstable intermediate compound is formed which exists for only a very short time and then breaks up to form two molecules of hydrogen iodide:



The bonds holding the atoms together in the intermediate body (or *complex*) are shown as dotted lines because they are evidently not the same as normal covalent bonds, in fact it is not known exactly what form they take. The complex is very unstable, and decomposes within an extremely short time of being formed.

It can now be seen that the energy that is absorbed during the reaction, as deduced from Le Chatelier's principle, must be the amount of energy required to form the complex. The latter is called an *activated complex* since it contains this additional energy, and the quantity of energy required to form it is the *activation energy*. This energy is re-emitted when the complex decomposes, so that the final heat of reaction depends only on the nature of the reactants and the products. This is illustrated by the energy diagram shown in Fig. 80. Lines A and B represent the

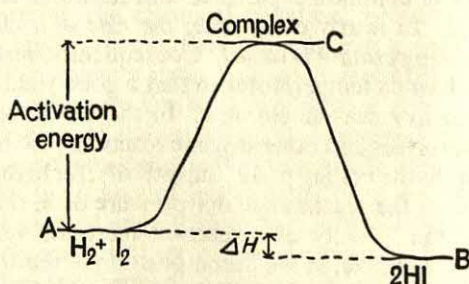


Fig. 80. Energy of activation

relative energies of the reactants and products, A being the total energy of one mole of H_2 plus one mole of I_2 , and B the energy of two moles of HI . When the reaction is over, the energy will have altered by an amount equal to the difference between A and B, and this difference is equal to the heat of reaction. In this particular reaction the products have a lower energy than the reactants, so that heat is evolved (exothermic) and ΔH is negative. The curved line shows the actual path of the reaction via the activated complex, which is at the much higher energy level C. Molecules of hydrogen and iodine can only surmount this energy barrier when they have acquired an additional amount of energy equal to the activation energy.

We must next see where this additional energy comes from. It has

been shown (§ 4.3) that the kinetic energy of the molecules in a gas is not evenly distributed, because there is a continual exchange of energy during collisions. The energy distribution curves in Fig. 18 (p. 55) show that there is a definite proportion of molecules with energies greater than a particular value, and that this proportion increases as the temperature is raised. If the activation energy is large, the proportion of molecules which have sufficient energy to form the complex may be very small, and this explains why only a minute fraction of the total number of collisions actually results in reaction taking place. At a higher temperature, the number of successful collisions will be greater, so that the reaction velocity is increased.

12.4. The measurement of reaction rates

While a chemical reaction is taking place, the reactants are being used up and their concentration therefore steadily decreases. Since the reaction velocity is proportional to the concentration of the reactants, it follows that the velocity also decreases with time, and a plot of concentration against time gives the type of curve shown in Fig. 81.

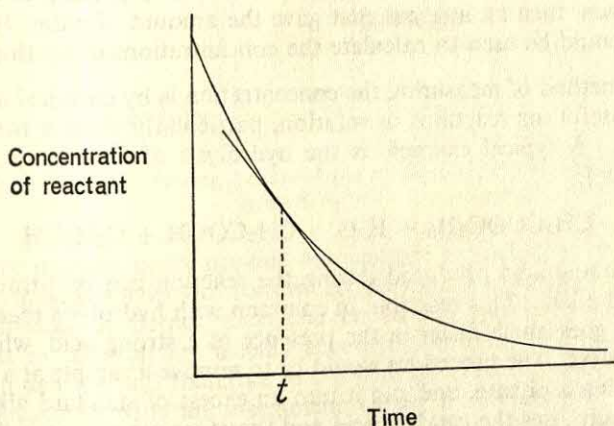


Fig. 81. Change of reaction velocity with time. The gradient of the tangent shows the rate at time t

The actual rate at any time could be found by drawing a tangent to the curve, as shown. However, this is not a very accurate method, and the velocity constant is usually calculated mathematically from the measured values of the concentration at definite times (see §§ 12.6 and 12.7).

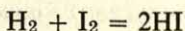
The experimental measurement of reaction rates is based on the following points:

(a) *Temperature.* Since reaction rates vary greatly with temperature, the reaction must be carried out at a definite and carefully controlled temperature. The actual temperature selected must be such that the

reaction goes at a reasonable speed, and this will decide whether the experiment is conducted in a thermostat bath or (for higher temperatures) in a temperature-controlled furnace.

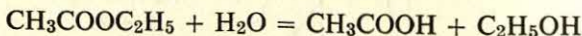
(b) *The reaction must be started at a definite time.* Where there are two reactants (or one reactant and a catalyst), the two can be brought to the required temperature in separate vessels and mixed at the same time as a clock is started. If there is only one reactant, this is kept well below the reaction temperature (so that the amount of reaction taking place is negligible) and then heated rapidly; the time when its temperature reaches the required value is then taken as the start of the reaction.

(c) *Concentration measurements are made at definite time intervals.* It is usually sufficient to measure the concentration of only one substance, which may be either a reactant or a product: the amounts of the other constituents can be deduced from the chemical equation. Thus in the reaction



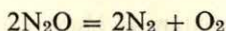
for every two moles of HI that are produced, one mole each of H_2 and I_2 is used up. If the amounts of H_2 and I_2 present at the start are known, then an analysis that gave the amount of either H_2 or I_2 , or HI, could be used to calculate the concentrations of all three.

One method of measuring the concentration is by chemical analysis: this is useful for reactions in solution, particularly when a titration is possible. A typical example is the hydrolysis of an ester (e.g. ethyl ethanoate):

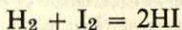


The ethanoic acid produced during the reaction can be titrated with standard alkali. This reaction, in common with hydrolysis reactions in general, goes much faster in the presence of a strong acid, which acts as a catalyst. The procedure would be to remove a sample at a definite time, using a pipette, and run it into an excess of standard alkali; the latter neutralises the catalyst acid and therefore almost stops the reaction, thus fixing the time interval. If the excess alkali is then titrated with standard acid, the total amount of acid in the sample can be calculated. The catalyst acid is not used up during the reaction, and therefore has a constant concentration throughout the reaction. When this is subtracted from the total acid, the amount of ethanoic acid in the sample is found. If a reaction cannot be stopped quickly in this manner, an alternative method is to cool the sample by running it into a large volume of cold water, thus considerably reducing the rate of reaction.

Gaseous reactions can sometimes be followed by means of pressure measurements, using the type of apparatus shown in Fig. 82. This method applies to reactions where there is a change in the number of molecules, e.g. the decomposition of dinitrogen oxide when heated:



There are three molecules of products produced for every two molecules of dinitrogen oxide that react, so that the pressure increases; the amount of decomposition that has occurred can be calculated from the total pressure. The method cannot be applied to reactions where there are equal numbers of gaseous molecules on both sides of the equation, for example in the reaction



when two molecules of the reactants are used up, two molecules of products are formed and the pressure does not alter.

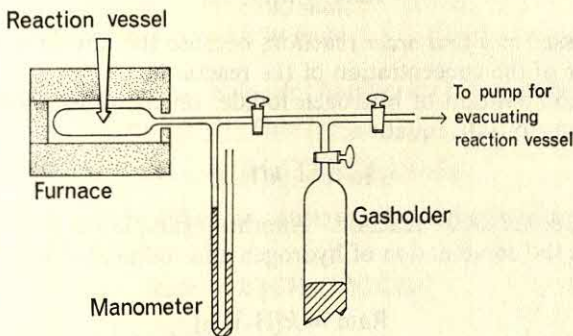
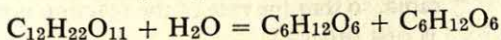


Fig. 82. Apparatus for measuring the rate of a gaseous reaction by means of pressure measurements

Pressure measurements provide an example of the use of physical measurements to follow concentration changes. Other physical properties may also be used, *e.g.* density. Reactions in solution are usually accompanied by a small change in density, and therefore in the volume. The change can be measured with an instrument called a *dilatometer* (Fig. 83) by means of the rise or fall of the meniscus in a narrow capillary tube.

Ionic reactions in solution usually cause a change in electrical conductance, which can be followed if the reaction is contained in a suitable cell.

Another useful physical measurement is that of optical rotation. It can be used for reactions involving *optically active* compounds, *i.e.* those that have the property of rotating the plane of polarised light. An example is the hydrolysis of sucrose, the products being glucose and fructose:



Sucrose rotates polarised light to the right (*dextro*-, or

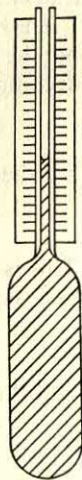


Fig. 83. Dilatometer

(+)-rotatory) whilst the mixture of glucose and fructose rotates it to the left (*laevo*-, or (-)-rotatory). For this reason the reaction is known as the "inversion" of sucrose.

12.5. The order of reaction

When the rate of a reaction has been measured, the results give the concentrations of the reactants at the start and at certain times during the reaction. In order to calculate the velocity constant, the equation that connects the rate of the reaction with the concentration must be known. For example, the rate at which dinitrogen pentoxide decomposes on heating is found to fit the equation:

$$\text{Rate} = k[\text{N}_2\text{O}_5]$$

This is classed as a *first order* reaction, because the rate depends on the first power of the concentration of the reactant.

The decomposition of hydrogen iodide, on the other hand, gives a different type of rate equation:

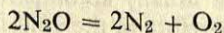
$$\text{Rate} = k[\text{HI}]^2$$

This is a *second order* reaction. Another example of a second order reaction is the combination of hydrogen and iodine, for which the rate is given by:

$$\text{Rate} = k[\text{H}_2][\text{I}_2]$$

The last two equations are mathematically similar, because they both contain the product of two concentration terms. The order of reaction is defined as *the sum of the powers to which the concentrations are raised*.

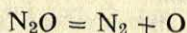
The order of a reaction has to be determined experimentally: it cannot be deduced from the chemical equation. Thus dinitrogen oxide decomposes according to the equation:



but the reaction is found to be first order, *i.e.*:

$$\text{Rate} = k[\text{N}_2\text{O}]$$

This is because the reaction takes place in two separate stages. In the first step, a molecule of dinitrogen oxide decomposes,



and the atoms of oxygen then combine:



The second step is very rapid, so that the rate of the reaction is governed by the first step, which is first order.

The majority of chemical reactions are found to be complex, some of

them involving a large number of separate steps. Many of them have orders which are not a whole number, for example orders of $\frac{1}{2}$ or $\frac{3}{2}$ are not uncommon. However, a large number of reactions, both simple and complex, are either first or second order.

The order of a reaction is sometimes altered by the conditions. An example of this is a reaction between two different substances when one reactant is present in large excess. Suppose an ester to be hydrolysed with an excess of water (say 100 moles of water to one mole of ester). The reaction will go virtually to completion, and the amounts of the various constituents at the start and finish will be as follows:

	$\text{CH}_3\text{COOCH}_3$	+	H_2O	=	CH_3COOH	+	CH_3OH
<i>Start</i>	1 mole		100 mole		0		0
<i>Finish</i>	0		99 mole		1 mole		1 mole

The concentration of water molecules hardly alters during the course of the reaction, so that in the rate equation

$$\text{Rate} = k[\text{CH}_3\text{COOCH}_3][\text{H}_2\text{O}]$$

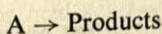
the term $[\text{H}_2\text{O}]$ can be taken as constant. The equation can therefore be written

$$\text{Rate} = k'[\text{CH}_3\text{COOCH}_3]$$

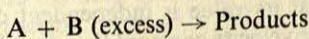
and the reaction is first order.

12.6. First order reactions

These can be represented by the following general types:



or



In each case the reaction rate is given by

$$\text{Rate} = k[\text{A}]$$

and since the rate is equal to that at which A is used up,

$$-\frac{d[\text{A}]}{dt} = k[\text{A}]$$

where t = time. Let the initial concentration of A be c_0 , and the concentration after a time t seconds be c . Substituting in the above equation,

$$-\frac{dc}{dt} = kc$$

The reaction rate is given by

$$\text{Rate} = k[A][B]$$

or (for the second type)

$$\text{Rate} = k[A]^2$$

Using the same symbols as before, at time t the concentrations of both A and B are equal to c , so that both equations become:

$$-\frac{dc}{dt} = kc^2$$

or

$$k dt = -\frac{dc}{c^2}$$

This equation integrates as follows:

$$k \int dt = - \int \frac{dc}{c^2}$$

$$kt = \frac{1}{c} + \text{Constant}$$

When $t = 0$, $c = c_0$, so that:

$$0 = \frac{1}{c_0} + \text{Constant}$$

$$\text{Constant} = -\frac{1}{c_0}$$

Substituting this value for the constant in the previous equation:

$$kt = \frac{1}{c} - \frac{1}{c_0}$$

$$= \frac{c_0 - c}{c_0 c}$$

$$k = \frac{1}{t} \frac{c_0 - c}{c_0 c}$$

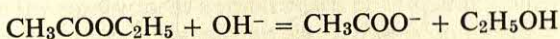
The value of k for a second order reaction can be calculated from the above equation, and will be seen to depend on the units of both time and concentration (usually given in seconds and mol dm^{-3}). The half-life can be found by putting $c = c_0/2$:

$$t_1 = \frac{1}{k} \frac{c_0 - c_0/2}{c_0 \times c_0/2}$$

$$= \frac{1}{kc_0}$$

so that the half-life is inversely proportional to the initial concentration (compare this with the half-life of a first order reaction, which is independent of concentration).

Examples of second order reactions are the combination of hydrogen and oxygen, and the decomposition of hydrogen iodide (p. 192); also, the hydrolysis of an ester in alkaline solution:



The hydroxyl ions act as a catalyst, but are used up because they react with the ethanoic acid produced by the reaction. If the alkali used is caustic soda, the products will be sodium ethanoate and ethanol, and the rate of reaction will be:

$$\text{Rate} = k[\text{CH}_3\text{COOC}_2\text{H}_5][\text{OH}^-]$$

12.8. Finding the reaction order

It should now be clear that the velocity constant cannot be calculated until the order of reaction is known. The latter can be determined by using one of the following methods.

Trial method

This consists in applying the two kinetic equations (first order and second order) to the experimental results, and finding which of them gives a constant value for the velocity constant. This may be done either by calculating k for each separate measurement or by plotting a graph. Since the initial concentration c_0 is a constant for each complete experiment, the first order equation reduces to:

$$t = -\frac{2.3}{k} \log_{10} c + \text{Constant}$$

so that if $\log_{10} c$ is plotted against t a straight line is obtained if the reaction is first order. The second order equation can be put in the form:

$$t = \frac{1}{k} \frac{1}{c} + \text{Constant}$$

and in this case a plot of $1/c$ will give a straight line.

When the order has been decided, the value of k can be calculated from the slope of the line.

Half-life method

It has been shown that the half-life is independent of the initial concentration for a first order reaction, but inversely proportional to it for a reaction of the second order. If separate experiments are carried out, starting with different concentrations of the reactant, the order can be determined by finding the time taken to complete a certain fraction

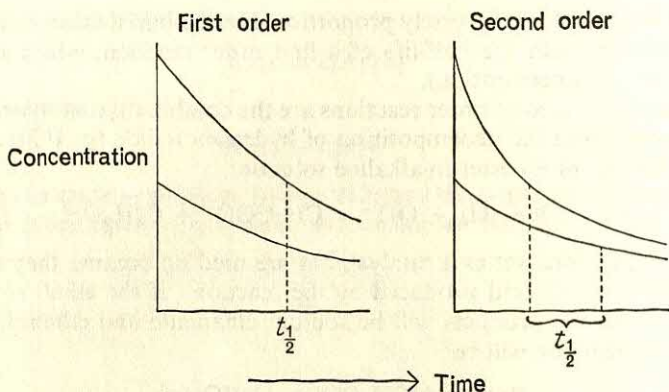


Fig. 84. Times of half change for first and second order reactions

(not necessarily half) of the reaction. If chemical analysis is being used to follow the change in concentration, the results must be plotted against time (see Fig. 84). When a physical measurement is used (e.g. pressure), it is only necessary to find the time at which the reading corresponds to the desired amount of reaction.

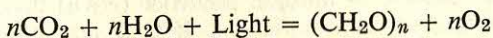
12.9. Photochemical reactions

The rates of some chemical reactions are greatly influenced by light or ultra-violet radiation. A mixture of hydrogen and chlorine, for example, does not react at any measurable speed when in the dark, but in bright light hydrogen chloride is formed very rapidly. We have seen that reactions only take place when a certain quantity of energy (the activation energy) is available. In all the cases considered so far, this energy is supplied from the internal energy of the molecules: since the internal energy depends on the temperature, these are called *thermal reactions*. In *photochemical reactions* the energy is supplied by the radiation (Greek *photos*, "light").

According to the quantum theory (p. 18), radiation behaves as though it were a succession of small parcels, or quanta, of energy. If a molecule absorbs a quantum of radiation, it gains a definite amount of energy; if the latter is large enough, a chemical reaction may take place. The shorter the wavelength of the radiation, the larger will be the energy quanta, in accordance with Planck's equation. This explains why some photochemical reactions take place with ordinary light, while others (requiring a higher energy) need the shorter wavelength ultra-violet radiation.

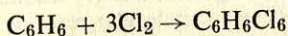
The most important photochemical reaction is the *photosynthesis* that takes place in plants, whereby carbon dioxide from the atmosphere is combined with water to form sugars as a first step in the production of more complicated carbohydrates. The light that falls on the leaves

of plants is absorbed by a substance called chlorophyll, which then causes the energy to be used in the photosynthesis reaction:



Photography is also a photochemical process. The light that falls on the film causes a reaction in the small crystals of silver bromide present in the emulsion, as a result of which specks of silver are formed. These specks can be enlarged by the action of a reducing agent (the *developer*), thus giving the negative image of the object that has been photographed.

An example of an industrial photochemical reaction is the production of benzene hexachloride by the chlorination of benzene, using ultra-violet radiation:



QUESTIONS

G.C.E.

1. (a) Define the term *order of a reaction*. (b) In an experimental study of a reaction in solution between two compounds *A* and *B*, the following information was obtained for the *initial* rate of the reaction:

Initial rate in $\text{mol dm}^{-3} \text{ s}^{-1}$	Initial concentrations of <i>A</i> and <i>B</i> in mol dm^{-3}	
	<i>A</i>	<i>B</i>
1.0×10^{-4}	1.0×10^{-1}	1.2×10^{-1}
4.0×10^{-4}	2.0×10^{-1}	1.2×10^{-1}
8.0×10^{-4}	2.0×10^{-1}	2.4×10^{-1}

What is the order of the reaction with respect to (i) the reactant *A*, (ii) the reactant *B*?

(c) The decomposition of benzene diazonium chloride in aqueous solution is a reaction of the first order which proceeds according to the equation $\text{C}_6\text{H}_5\text{N}_2\text{Cl} = \text{C}_6\text{H}_5\text{Cl} + \text{N}_2(\text{g})$. A certain solution of benzene diazonium chloride contains initially an amount of this compound which gives 80 cm^3 of nitrogen on complete decomposition. It is found that, at 30°C , 40 cm^3 of nitrogen are evolved in 40 minutes. How long after the start of the decomposition will 70 cm^3 of nitrogen have been evolved? [All volumes of nitrogen refer to the same temperature and pressure.] [Oxford]

2. Define, or explain, the terms *rate* and *order of a reaction*.

(a) Describe and explain carefully in terms of molecular collision theory the effect of temperature change on the rate of a homogeneous gaseous reaction.

(b) For the exothermic gaseous reaction $\text{A}_2(\text{g}) \rightarrow 2\text{A}(\text{g})$ sketch graphs to show the course of the decomposition (dissociation) by plotting the concentrations of A_2 and *A* against time. Using the same scale on another graph, plot the concentration of A_2 against time to show what happens in similar experiments in which (i) the temperature is raised, (ii) the pressure is lowered, (iii)

a suitable catalyst is introduced. Add a brief statement in each case to clarify your answer.

(c) The decomposition of nitrogen pentoxide (N_2O_5) dissolved in tetrachloromethane (carbon tetrachloride) at 45°C is *first* order. Using the concentrations of nitrogen pentoxide and the times given, estimate by a graphical method the rate constant for the decomposition, stating the units in which it is expressed.

time/s	0	250	500	750	1000	1500	2000	2500
concentration/ mol dm^{-3}	2.33	1.95	1.68	1.42	1.25	0.95	0.70	0.50

[S.U.J.B.]

3. Explain the terms *order*, *molecularity* and *stoichiometry* when applied to a chemical reaction. Give **one** example each of reactions which are (a) zero order with respect to one component and (b) second order overall. Explain the circumstances when (a) a unimolecular reaction can show second-order reaction kinetics and (b) a bimolecular reaction can show first-order kinetics.

An experiment on the reaction of benzoyl chloride with phenylamine (aniline), starting with equal concentrations of reactants, gave the following results.

Time in minutes	0	5	10	20	30
Concentration of phenylamine/ mol dm^{-3}	0.0200	0.0133	0.0100	0.0069	0.0051

Determine the reaction order and the velocity constant.

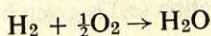
[O. & C., "S"]

CHAPTER 13

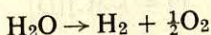
CHEMICAL EQUILIBRIUM

13.1. Reversible reactions

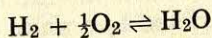
We often say that a chemical reaction goes "to completion." Thus if hydrogen, mixed with exactly half its own volume of oxygen, is exploded by means of an electric spark, there is apparently complete conversion into water:



However, if water (or rather steam) is heated to a very high temperature it will decompose to an appreciable extent into hydrogen and oxygen, thus showing that the reaction can also take place in the reverse direction:

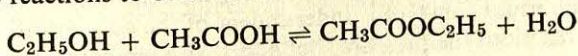


It is probable, in fact, that all chemical reactions can take place in either direction, *i.e.* they are *reversible*. In the above reaction, it so happens that at room temperature the amounts of hydrogen and oxygen left at the end of the reaction are too small to be detected, so that for all practical purposes it can be assumed that the reaction has gone to completion. The term *reversible reaction* is therefore normally applied to reactions where both the forward and reverse reactions take place to a measurable extent. This is indicated in the chemical equation by the use of double arrows; for example the hydrogen-oxygen reaction at high temperatures would be written:



13.2. The dynamic nature of equilibrium

Whenever two opposing processes occur in an enclosed system, a state of equilibrium will eventually be reached. Examples of equilibrium in physical systems have already been given (*e.g.* vapour pressure), and the same principle applies to chemical reactions. One of the first reversible reactions to be studied was the esterification of ethanol:



A mixture of ethanol and ethanoic acid will react to form ethyl ethanoate and water, but the reaction does not go to completion: after a time, the concentrations of all four substances reach constant values. This is the point at which equilibrium has been established between the forward

and reverse reactions. Exactly the same position would be reached if, instead of ethanol and ethanoic acid, the starting point was ethyl ethanoate and water.

We can tell when a reaction has reached equilibrium by the fact that there is no further change in the composition of the mixture. This does not mean that all chemical reaction has stopped, because the two opposing reactions are, in fact, still taking place. What has happened is that the rates of the two reactions have become equal, and this is why equilibrium is said to be a *dynamic* process.

Guldberg and Waage (1879) applied the idea of a dynamic equilibrium in the following way. In the reversible reaction:



the rate of the forward reaction (v_1) is given by:

$$v_1 = k_1[A][B]$$

where k_1 is the rate constant for this reaction. Similarly, the rate of the reverse reaction (v_2) is:

$$v_2 = k_2[C][D]$$

If the reaction is started with a mixture of A and B, then the rate v_1 will steadily decrease as these are used up. At the same time, the rate v_2 of the reverse reaction will increase as more C and D are formed. At some point the rates of the two reactions must become equal, and after that there will be no further change in the concentration of any of the substances present, *i.e.* the reaction will be in a state of equilibrium. Therefore, at equilibrium $v_1 = v_2$. Hence:

$$k_1[A][B] = k_2[C][D]$$

$$\frac{k_1}{k_2} = \frac{[C][D]}{[A][B]}$$

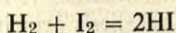
The ratio k_1/k_2 may be replaced by a single constant, thus giving:

$$K = \frac{[C][D]}{[A][B]}$$

K is known as the *equilibrium constant*, and the equation is a mathematical statement of Guldberg and Waage's *law of mass action*. The law may also be stated as follows: *the extent of a chemical reaction is proportional to the molar concentrations of the reacting substances.*

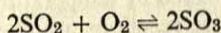
The equilibrium constant is independent of the concentration or (for a gaseous reaction) the pressure, but alters with temperature. It will be seen that the concentration terms for the products are written in the numerator, and those of the reactants in the denominator (*i.e. products over reactants*). This convention is adopted so that the equilibrium constant of any particular reaction is always written in the same way.

If more than one molecule of any reactant or product appears in the chemical equation, the concentration must be raised to the appropriate power, thus:



$$K = \frac{[\text{HI}]^2}{[\text{H}_2][\text{I}_2]}$$

In the case of gaseous reactions, it is more convenient to express the concentrations in terms of the partial pressures of the different substances, and the equilibrium constant is then written K_p . The equilibrium constant in terms of molar concentrations is usually written K_c . Thus for the gaseous reaction



the equilibrium constant could be written in either of the following ways:

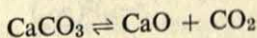
$$K_c = \frac{[\text{SO}_3]^2}{[\text{SO}_2]^2[\text{O}_2]}$$

$$K_p = \frac{(p_{\text{SO}_3})^2}{(p_{\text{SO}_2})^2(p_{\text{O}_2})}$$

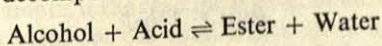
The numerical value of K depends on the concentration units and so for most reactions K_c and K_p have different values.

The kinetic approach to equilibrium used by Guldberg and Waage cannot, strictly speaking, be applied to all reactions, because the rate of a reaction does not always follow simply from the chemical equation (this was discussed in the previous chapter). However, it is found by experiment that the law of mass action applies to *all* chemical reactions. Moreover, it can be deduced quite independently from thermodynamics.

Equilibrium conditions can only arise when the reacting system is enclosed, *i.e.* when none of the reactants or products can escape. If one or more of the products is continuously removed, then the reaction will continue to completion: this is one way of increasing the yield from a reversible reaction. In the manufacture of quicklime by heating limestone:



the carbon dioxide is removed with a current of air, so that all the limestone can be decomposed. In esterification reactions:



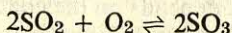
and in many other reactions where water is one of the products, the water may be removed by means of a dehydrating agent (*e.g.* anhydrous aluminium sulphate or concentrated sulphuric acid) to give a greater yield of the products.

13.3. How equilibrium is affected by temperature, pressure and catalysts

A change in temperature causes the equilibrium constant to alter. The direction of the change—*i.e.* whether K increases or decreases—can be found by applying Le Chatelier's principle (p. 101). If the temperature is raised, the equilibrium will alter so as to oppose the change *i.e.* heat will be absorbed. If the reaction is exothermic, it can only absorb heat when it takes place in the reverse direction, so that the concentrations of the products will decrease and the concentrations of the reactants will increase. This means that the equilibrium constant (products over reactants) will become smaller. An endothermic reaction absorbs heat when proceeding in the forward direction, so that K increases if the temperature is raised.

The reason why K is affected by temperature is that the rates of both the forward and the reverse reactions are altered, but not to the same extent. Since the velocity of a reaction is increased by a rise in temperature, it also follows that equilibrium is more quickly attained at a higher temperature.

When reversible reactions involve gases, the composition of the equilibrium mixture may be altered if the total pressure of the mixture is changed. This is not due to any change in the value of K , since the latter is independent of pressure. The direction of the change can again be predicted from Le Chatelier's principle. For the reaction:



for every two moles of SO_3 that are formed, a total of three moles of reactants are used up. All the substances are gaseous, so that when the forward reaction takes place there is a decrease in volume. If the total pressure is increased, the position of equilibrium will alter so as to oppose this change, *i.e.* there will be a decrease in volume. This means that there will be more SO_3 , and less of the reactants, in the equilibrium mixture.

The actual composition of the mixture at different pressures could be worked out as follows. The equilibrium constant for the reaction is given by:

$$K_p = \frac{(p_{\text{SO}_3})^2}{(p_{\text{SO}_2})^2(p_{\text{O}_2})}$$

The partial pressure of a gas in a mixture is related to the total pressure by the expression

$$p_{\text{SO}_3} = x_{\text{SO}_3}p$$

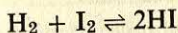
where x_{SO_3} is the mole fraction of SO_3 (*i.e.* the number of moles of SO_3 divided by the total numbers of moles of all the gases present), and p is the total pressure (*see* § 5.3). Substituting for partial pressures in the equilibrium constant expression:

$$K_p = \frac{(x_{\text{SO}_3})^2 p^2}{(x_{\text{SO}_2})^2 p^2 (x_{\text{O}_2}) p}$$

$$= \frac{(x_{\text{SO}_3})^2}{(x_{\text{SO}_2})^2 (x_{\text{O}_2})} \frac{1}{p}$$

Since K_p must remain constant, then if the pressure is increased the proportion of SO_3 in the mixture will be greater and the proportions of SO_2 and O_2 smaller.

There are certain reactions where the equilibrium is not affected by a change in pressure. This happens when there are equal numbers of gaseous molecules on both sides of the equation, as in the reaction:



Here there is no volume change when the reaction takes place in either direction, and the equilibrium quantities are independent of the total pressure.

Reactions are often speeded up by using a suitable catalyst (see Chapter 16). In the case of a reversible reaction, the catalyst increases the rates of both the forward and the reverse reactions, but in exactly the same proportion. The result is that the equilibrium constant is not altered but the time taken for equilibrium to be reached may be considerably reduced.

The points covered above may be summarised as follows:

(a) *Effect of temperature.* If the temperature is raised, the equilibrium constant of an exothermic reaction will decrease in value, while that of an endothermic reaction will increase. A fall in temperature will, of course, have the reverse effect.

(b) *Effect of pressure.* The equilibrium constant is unaffected by pressure, but if there are gases present the composition of the equilibrium mixture may alter. An increase in pressure causes a change in the direction which corresponds with a decrease in volume, and vice versa. If there are equal numbers of gaseous molecules on both sides of the equation, a change in pressure has no effect.

(c) *Effect of catalysts.* The presence of a catalyst causes no change in either the equilibrium constant or the composition of the mixture, but speeds up the attainment of equilibrium.

It is often necessary to decide the best conditions for carrying out a reversible reaction, so as to obtain a good yield of the products within a reasonable time. The points mentioned above may all have to be considered; for example, if the reaction is exothermic a low temperature will favour a high value for the equilibrium constant, and therefore a good yield of products. However, the reaction may then become very slow. A suitable catalyst might be used to increase the speed, or (if the reaction is gaseous) it might be possible to increase the yield by working at a high pressure.

Some examples of reversible reactions, and their equilibrium conditions, will now be given. They will be divided into the following groups:

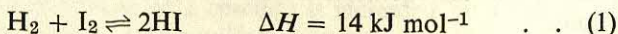
Homogeneous gaseous equilibria, in which all the substances are gases and therefore in the same phase.

Homogeneous liquid equilibria, where the substances are all in the liquid phase. This includes reactions in solution.

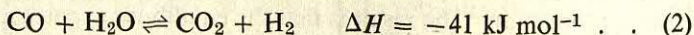
Heterogeneous equilibria, where there are two or more separate phases present. Such reactions usually involve solids and gases.

13.4. Homogeneous gaseous reactions

We shall first study two examples of reactions where there is no change in the total number of molecules. The first is the formation of hydrogen iodide:



and the second is an industrially important reaction in which steam reacts with carbon monoxide at a high temperature:



The equilibrium constants, in partial pressures, are:

$$(1) \quad K_p = \frac{(p_{\text{HI}})^2}{(p_{\text{H}_2})(p_{\text{I}_2})}$$

$$(2) \quad K_p = \frac{(p_{\text{CO}_2})(p_{\text{H}_2})}{(p_{\text{CO}})(p_{\text{H}_2\text{O}})}$$

Since reaction (1) is endothermic, a rise in temperature would cause the equilibrium constant to increase in value, thus giving a higher proportion of HI in the equilibrium mixture. Reaction (2) is exothermic, so that a lower temperature would favour a higher yield of the products.

As there is an equal number of pressure terms in the numerator and denominator of the equilibrium constant for both these reactions, K_p is a pure number and is independent of the units in which the pressures are measured. For the same reason, the partial pressures may be replaced by any term that is proportional to the pressure, *e.g.* numbers of moles, or molar concentration. This can be demonstrated by substituting, for the partial pressures, the mole fraction $\times$ the total pressure p , *e.g.*

$$\begin{aligned} p_{\text{CO}} &= x_{\text{CO}} p \\ &= \frac{n_{\text{CO}}}{n} p \end{aligned}$$

where n_{CO} is the number of moles of CO and n is the total number of moles of all substances present. Substitution now gives for reaction (2):

$$K_p = \frac{\left(\frac{n_{\text{CO}_2}}{n} \times p\right) \left(\frac{n_{\text{H}_2}}{n} \times p\right)}{\left(\frac{n_{\text{CO}}}{n} \times p\right) \left(\frac{n_{\text{H}_2\text{O}}}{n} \times p\right)}$$

$$= \frac{n_{\text{CO}_2} \times n_{\text{H}_2}}{n_{\text{CO}} \times n_{\text{H}_2\text{O}}}$$

Dividing each term by the total volume (V) will not alter the value of K_p :

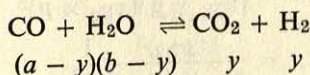
$$K_p = \frac{\left(\frac{n_{\text{CO}_2}}{V}\right) \left(\frac{n_{\text{H}_2}}{V}\right)}{\left(\frac{n_{\text{CO}}}{V}\right) \left(\frac{n_{\text{H}_2\text{O}}}{V}\right)}$$

and since the number of moles of a substance divided by the volume is equal to the molar concentration:

$$K_p = \frac{[\text{CO}_2][\text{H}_2]}{[\text{CO}][\text{H}_2\text{O}]} = K_c$$

Hence, for gaseous reactions with equal numbers of molecules on either side of the equation, the equilibrium concentrations can be expressed as partial pressures, molar concentrations, or simply numbers of moles. K_p and K_c are therefore identical.

In the practical application of equilibrium constants, it is often necessary to calculate the composition of the final equilibrium mixture when starting with certain concentrations of reactants (sometimes one of the products may also be present at the beginning). Suppose, for example, that in the above reaction there had been a moles of carbon monoxide and b moles of steam initially; let the amounts of carbon dioxide and hydrogen formed when equilibrium is reached be y moles of each. The composition of the mixture is then:



This gives K_p (or K_c) as:

$$K_p = \frac{y^2}{(a - y)(b - y)}$$

from which, knowing the value of K_p , y can be calculated.

EXAMPLE

If a mixture of carbon dioxide and steam in the proportion of 1:2 by volume is heated to 400°C, at which temperature the equilibrium constant is 1.29, what will be the composition of the equilibrium mixture?

Since the volume of a gas is proportional to the number of moles present, we can put $a = 1$, and $b = 2$. Substituting in the equation for K_p given above:

$$1.29 = \frac{y^2}{(1-y)(2-y)}$$

$$1.29(2 - 3y + y^2) = y^2$$

$$0.29y^2 - 3.87y + 2.58 = 0$$

$$y = \frac{3.87 \pm \sqrt{3.87^2 - 4 \times 0.29 \times 2.58}}{2 \times 0.29}$$

$$= 0.71 \text{ (or } 12.6, \text{ which is impossible)}$$

The composition of the mixture will therefore be as follows:

$$\left. \begin{array}{ll} \text{CO} & 1 - 0.71 = 0.29 \\ \text{H}_2\text{O} & 2 - 0.71 = 1.29 \\ \text{CO}_2 & 0.71 \\ \text{H}_2 & 0.71 \end{array} \right\} \text{parts by volume}$$

Some examples will now be given of gaseous reactions where there is a change in the number of molecules. In reactions of this type the composition of the equilibrium mixture is affected by the total pressure, and K_p is not equal in value to K_c .

In the production of ammonia from nitrogen and hydrogen there is the equilibrium:



for which the equilibrium constant will be

$$K_p = \frac{(p_{\text{NH}_3})^2}{p_{\text{N}_2} \times (p_{\text{H}_2})^3}$$

Replacing partial pressures by mole fractions multiplied by the total pressure:

$$\begin{aligned} K_p &= \frac{(x_{\text{NH}_3} \times p)^2}{(x_{\text{N}_2} \times p)(x_{\text{H}_2} \times p)^3} \\ &= \frac{(x_{\text{NH}_3})^2}{x_{\text{N}_2} \times (x_{\text{H}_2})^3} \frac{1}{p^2} \end{aligned}$$

Since this reaction is exothermic and results in a decrease in the number of gaseous molecules, Le Chatelier's principle predicts that the proportion of ammonia in the equilibrium mixture will be increased (a) by lowering the temperature, and (b) by increasing the pressure. However, the reaction takes place too slowly below about 400°C, even in the presence of a catalyst, and at this temperature the equilibrium constant is very small. To increase the yield of ammonia a high pressure (usually about 2.5×10^7 Pa) is therefore used.

The actual proportion of ammonia in the mixture at any particular pressure can be calculated from the above equation. The following example is worked the other way round to simplify the algebra.

EXAMPLE

The equilibrium constant for the ammonia synthesis reaction is $K_p = 4.24 \times 10^{-15} \text{ Pa}^{-2}$ at 450°C . What pressure is required to obtain a mixture containing 10% of ammonia by volume, starting with a mixture of hydrogen and nitrogen in the proportions of 3:1?

The mole fraction of each gas in the equilibrium mixture will be equal to its proportion by volume. Ammonia accounts for 0.1 of the total, the remaining 0.9 being made up of hydrogen and nitrogen still in their original proportions:

Ammonia	0.1	$x_{\text{NH}_3} = 0.1$
Hydrogen	$\frac{3}{4} \times 0.9 = 0.675$	$x_{\text{H}_2} = 0.675$
Nitrogen	$\frac{1}{4} \times 0.9 = 0.225$	$x_{\text{N}_2} = 0.225$

$$K_p = \frac{(x_{\text{NH}_3})^2}{x_{\text{N}_2} \times (x_{\text{H}_2})^3} \frac{1}{p^2}$$

$$4.24 \times 10^{-15} = \frac{0.1^2}{0.225 \times 0.675^2} \frac{1}{p^2}$$

$$p = \sqrt{\frac{0.1^2}{4.24 \times 10^{-15} \times 0.225 \times 0.675^2}}$$

$$= 4.8 \times 10^6 \text{ Pa}$$

The ammonia reaction is actually carried out at a much higher pressure than that worked out in the above example, in order to obtain a higher proportion of ammonia in the mixture. At high pressures, gases depart considerably from ideal behaviour, and this causes the equilibrium constant to vary with pressure (at 10^8 Pa K_p is $5.47 \times 10^{-14} \text{ Pa}^{-2}$).

For reactions where there is a change in the number of molecules, K_p and K_c have different values: the relationship between them can be found as follows. If a gas mixture of volume V contains n_A moles of gas A, then the partial pressure of A is given by the ideal gas equation as:

$$p_A V = n_A RT$$

so that

$$p_A = \frac{n_A}{V} RT$$

$$= [A] RT$$

since n_A/V is the concentration of A. For a reaction $A \rightleftharpoons B + C$ the equilibrium constant in terms of partial pressures would be:

$$K_p = \frac{p_B \times p_C}{p_A}$$

$$= \frac{[B]RT \times [C]RT}{[A]RT}$$

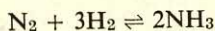
$$= K_c RT$$

In general, if a reaction causes an increase in the number of molecules equal to Δn , the relationship will be

$$K_p = K_c(RT)^{\Delta n}$$

EXAMPLE

Calculate the value of K_c for the ammonia equilibrium at 450°C , using the value of K_p from the previous example.



$$\Delta n = 2 - 4 = -2$$

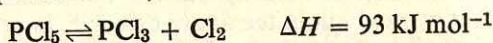
$$\begin{aligned} K_c &= \frac{K_p}{(RT)^{-2}} \\ &= K_p(RT)^2 \end{aligned}$$

Hence

$$\begin{aligned} K_c &= 4.24 \times 10^{-15} \times (8.31 \times 723)^2 \\ &= 1.53 \times 10^{-7} \text{ mol}^{-2} \text{ m}^6 \end{aligned}$$

where the concentration units are mol m^{-3} .

The next example is a dissociation reaction, the decomposition of phosphorus pentachloride, which is endothermic:



Application of Le Chatelier's principle shows that (a) increase in temperature will cause more PCl_5 to decompose, i.e. the value of the equilibrium constant will increase, and (b) an increase in the total pressure will decrease the extent of dissociation. The relation between the degree of dissociation α and the total pressure can be obtained in the following way:



Number of moles

$$(1 - \alpha) \quad \alpha \quad \alpha$$

$$\begin{aligned} K_p &= \frac{p_{\text{PCl}_3} \times p_{\text{Cl}_2}}{p_{\text{PCl}_5}} \\ &= \frac{x_{\text{PCl}_3} \times x_{\text{Cl}_2}}{x_{\text{PCl}_5}} p \end{aligned}$$

$$\text{Total number of moles} = (1 - \alpha) + \alpha + \alpha = 1 + \alpha$$

The mole fractions are:

$$x_{\text{PCl}_5} = \frac{1 - \alpha}{1 + \alpha} \quad x_{\text{PCl}_3} = x_{\text{Cl}_2} = \frac{\alpha}{1 + \alpha}$$

$$K_p = \frac{\frac{\alpha}{1 + \alpha} \times \frac{\alpha}{1 + \alpha}}{\frac{1 - \alpha}{1 + \alpha}} p$$

$$= \frac{\alpha^2}{(1 - \alpha)(1 + \alpha)} p$$

$$K_p = \frac{\alpha^2}{1 - \alpha^2} p$$

EXAMPLE

The value of K_p for the above reaction is 1.89×10^4 Pa at 200°C . Calculate the degree of dissociation at a pressure of 50 kPa.

$$1.89 \times 10^4 = \frac{\alpha^2}{1 - \alpha^2} 50\,000$$

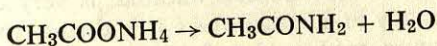
$$\alpha^2(1.89 + 5) = 1.89$$

$$\alpha = \sqrt{\frac{1.89}{6.89}}$$

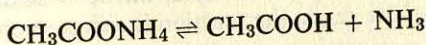
$$= 0.524$$

The degree of dissociation can be reduced by increasing the concentration of one of the products of the reaction. Thus if phosphorus pentachloride is heated in a vessel that already contains some chlorine gas, the partial pressure of PCl_5 in the equilibrium mixture is greater than if the chlorine had not been added. This can be seen from the equilibrium constant expression, remembering that K_p must remain constant: if p_{Cl_2} is increased, the ratio $p_{\text{PCl}_5}/p_{\text{PCl}_3}$ must increase in proportion.

Another example of suppression of dissociation is found in the preparation of acid amides by heating the ammonium salt of a fatty acid:



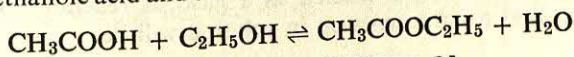
The dissociation of the ammonium salt



is reduced by adding an excess of fatty acid. Industrially, higher fatty acid amides are prepared by the same method but an excess of ammonia is used rather than an excess of fatty acid.

13.5. Homogeneous reactions in liquid systems

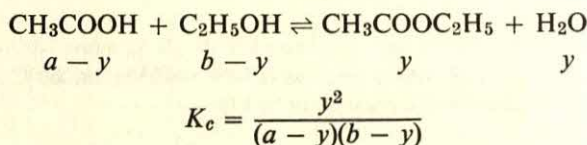
One of the earliest equilibrium systems studied was the reaction between ethanoic acid and ethanol:



$$K_c = \frac{[\text{CH}_3\text{COOC}_2\text{H}_5][\text{H}_2\text{O}]}{[\text{CH}_3\text{COOH}][\text{C}_2\text{H}_5\text{OH}]}$$

Since there is no change in the number of molecules when this reaction takes place, the molar concentrations can be replaced by the numbers

of moles of the constituents. Thus if a moles of acid and b moles of alcohol were taken at the start, and y moles of both ester and water had been formed at equilibrium, the equilibrium constant could be expressed as follows:



The equilibrium constant for this reaction is 4.0 and varies little with temperature, because the enthalpy of reaction is small.

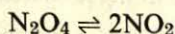
From the above equation it is possible to calculate the amount of ester that is formed from any given amounts of acid and alcohol. It is often important to obtain the best conversion of one reactant into the product of the reaction (*e.g.* acid $\rightarrow$ ester in this example) and the yield may be increased by taking an excess of the other reactant (in this case the alcohol), as shown by the following figures:

Number of moles of acid taken (a)	1	1	1	1	1
Number of moles of alcohol taken (b)	1	2	3	5	10
Moles of ester at equilibrium (y)	0.67	0.85	0.90	0.95	0.97

It is evident that there is little to be gained by taking more than about 3–5 moles of alcohol for each mole of acid.

The reverse reaction, *i.e.* the hydrolysis of the ester, is one example of an important type of reaction and one that is very common in the laboratory, especially in analysis where it is desired to break down a molecule into more readily identifiable parts. Other examples of hydrolysis reactions are: amide $\rightarrow$ acid, nitrile $\rightarrow$ acid, anilide $\rightarrow$ acid + amine. In all these cases, the reaction is more complete if an excess of water is used.

Reactions between inorganic substances in solution are mainly ionic in nature, and this type of equilibrium is dealt with separately in Chapter 14. An example of a molecular reaction in solution is the dissociation of dinitrogen tetroxide (N_2O_4):



This reaction can also be studied as a gaseous reaction. The equilibrium constant for the reaction in solution will be:

$$K_c = \frac{[\text{NO}_2]^2}{[\text{N}_2\text{O}_4]}$$

and the molar concentrations are equal to the number of moles divided by the volume of the solution V :

$$K_c = \frac{\left(\frac{n_{\text{NO}_2}}{V}\right)^2}{\left(\frac{n_{\text{N}_2\text{O}_4}}{V}\right)} = \frac{(n_{\text{NO}_2})^2}{n_{\text{N}_2\text{O}_4}} \frac{1}{V}$$

The equilibrium constant can also be related to the degree of dissociation. Suppose that there is present initially a concentration of N_2O_4 equal to c mol dm^{-3} , and that the degree of dissociation is α . The concentration in the equilibrium mixture will be:

$$\begin{aligned} \text{N}_2\text{O}_4 &\rightleftharpoons 2\text{NO}_2 \\ c(1 - \alpha) &\quad 2\alpha c \\ K_c &= \frac{(2\alpha c)^2}{c(1 - \alpha)} \\ &= \frac{4\alpha^2 c}{1 - \alpha} \end{aligned}$$

This equation can be used to calculate the equilibrium constant from measurements of α (e.g. by relative molecular mass determination).

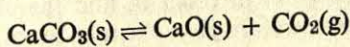
EXAMPLE

From a determination of relative molecular mass on a solution made by dissolving 1.1 mole of N_2O_4 in 1 dm^3 of trichloromethane, the degree of dissociation was found to be 0.0016 at 8°C . What is the value of K_c at this temperature?

$$\begin{aligned} K_c &= \frac{4 \times 0.0016^2 \times 1.1}{1 - 0.0016} \\ &= 1.1 \times 10^{-5} \text{ mol dm}^{-3} \end{aligned}$$

13.6. Heterogeneous equilibria

Heterogeneous reactions (i.e. those in which the reactants and products are in more than one phase) are mainly concerned with gas-liquid and gas-solid systems. The latter are the more common, and will be the only type covered here. A well-known example of such a reaction is the dissociation of calcium carbonate:



where there is one gas and two solids. We could write the equilibrium constant as:

$$K_c = \frac{[\text{CaO}][\text{CO}_2]}{[\text{CaCO}_3]}$$

We now have to decide what is meant by the "concentrations" of the calcium carbonate and the calcium oxide. These two solids will form

two separate phases, since it is unusual for solids to mix (see § 8.10). Any pure solid, at a particular temperature and pressure, will contain a constant number of molecules per unit volume, so that the molar concentration of a solid is a constant. Looking at it another way, we have seen that the vapour pressure of a liquid in a mixture is proportional to its molar concentration (§ 9.1): the vapour pressure of a pure liquid is constant, at a definite temperature, so that the concentration must also be a constant. A solid also has a vapour pressure, which is also constant for the pure solid. By analogy, we can use the vapour pressure of a solid as a measure of its concentration, and we shall then arrive at the same result, *i.e.* that the pure solid has a constant concentration. The actual value that is given to these constants does not matter provided that we always use the same values. By convention, *the concentration of a pure liquid or a pure solid is taken as unity*. The actual amount present has no effect on the concentration.

The equilibrium constant for the calcium carbonate reaction now becomes:

$$K_c = [\text{CO}_2]$$

and since we are now only dealing with the concentration of a gas, it is more convenient to use the pressure:

$$K_p = p_{\text{CO}_2}$$

The pressure of the CO_2 is also the total pressure of the system, since it is the only gas present. This is referred to as the *dissociation pressure*, and since it is equal to K_p it follows that the dissociation pressure has a definite value for any particular temperature. The pressure of the system is fixed and cannot be altered without upsetting the equilibrium.

The same information could also be obtained by applying the phase rule to this reaction. The number of phases is three (two solid, one gas) and the number of components, two. A little explanation is needed for the latter figure, since there are three separate chemical substances present. The phase rule, however, is concerned with *the smallest number of substances whose concentrations have to be known in order to find the composition of all parts of the system*. Since the three substances (CaCO_3 , CaO and CO_2) are in equilibrium, it is only necessary to know the concentrations of two of them in order to find the concentration of the third. The phase rule therefore gives the number of degrees of freedom as:

$$\begin{aligned} F &= C + 2 - P \\ &= 2 + 2 - 3 \\ &= 1 \end{aligned}$$

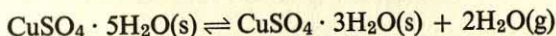
Only one of the two variables (temperature and pressure) can therefore be varied independently, so that if the temperature is fixed the pressure

must remain constant. Thus the phase rule gives exactly the same prediction as does the equilibrium constant.

The dissociation of calcium carbonate is endothermic, so that the equilibrium constant increases with increasing temperature as shown by the following figures:

Temperature (°C)	600	700	800	900
K_p (Pa)	245	2950	22 300	105 000

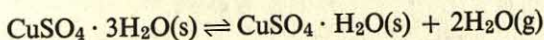
Another type of equilibrium involving two solids and one gas is the dissociation of salt hydrates. The ordinary form of copper(II) sulphate is the pentahydrate, which can lose water to form the trihydrate. In a closed vessel the following equilibrium is established:



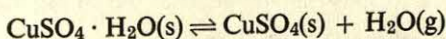
for which the equilibrium constant is

$$K_p = (p_{\text{H}_2\text{O}})^2$$

As before, the two solid phases do not appear in the expression. The equilibrium constant depends only on the pressure of water vapour, so that the latter will remain constant as long as some of both the hydrates are present. If water is removed from the system (*e.g.* by reducing the pressure and pumping off the water vapour) the pentahydrate will eventually all be converted into the trihydrate. A fresh equilibrium can then be established between the trihydrate and the next lower hydrate:



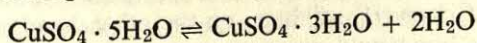
Finally, there can be equilibrium between the monohydrate and the anhydrous salt:



Each of these three equilibria has its own dissociation pressure, as shown in Fig. 85.

Salt hydrates that are exposed to the atmosphere often tend either to lose or to take up water, depending on whether their dissociation pressure is greater or less than the pressure of water vapour in the atmosphere. Hydrates that lose water are said to *effloresce* (meaning "to break out into flower"), the term being derived from the physical change that takes place owing to the breakdown of the crystal structure. This starts on the surface of the crystal, and leaves the material in the form of a powder.

The dissociation pressure of the equilibrium



is 1040 Pa at 25°C, while the average pressure of water vapour in the atmosphere is about 2000 Pa. Copper(II) sulphate pentahydrate (the

familiar blue crystals) do not, therefore, effloresce under normal atmospheric conditions. In very dry air, however, with a partial pressure of water vapour less than 1040 Pa, the pentahydrate would lose water until entirely converted into the trihydrate. No more water would be lost unless the partial pressure fell below 750 Pa, which is the dissociation pressure of the trihydrate.

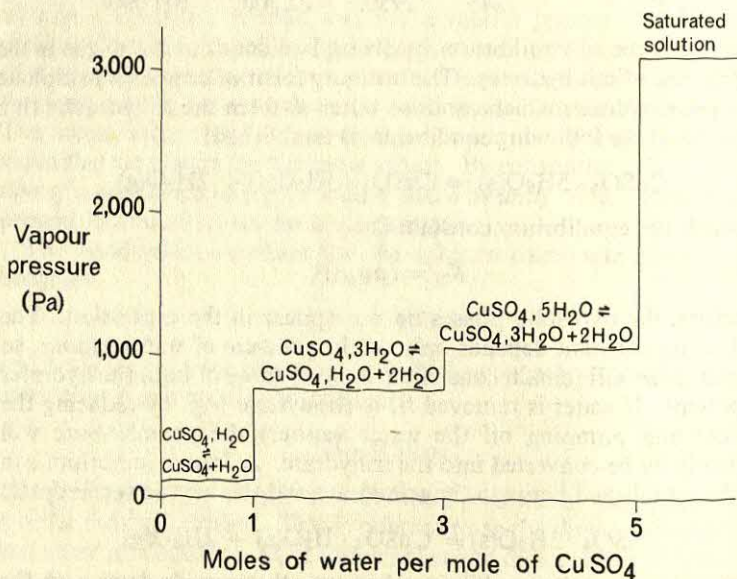
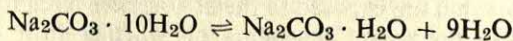


Fig. 85. Dissociation pressures of copper(II) sulphate hydrate systems

Some hydrates effloresce under all normal atmospheric conditions; for example, sodium carbonate crystals (decahydrate) have a dissociation pressure of 2400 Pa, the equilibrium being

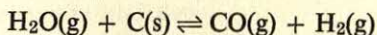


These crystals will therefore be converted to the monohydrate unless kept in an air-tight bottle.

Some substances take up water to form a solution, *i.e.* they *deliquesce* (meaning "become liquid"). This occurs when the vapour pressure of a saturated solution of the substance is less than the pressure of water vapour in the atmosphere. Calcium chloride is an example of a deliquescent salt, the vapour pressure of a saturated solution being only about 670 Pa. Copper(II) sulphate, on the other hand, will not deliquesce because this would require a water vapour pressure of 3100 Pa (see Fig. 85), corresponding to approximately 100% humidity.

Two examples of heterogeneous reactions of industrial importance

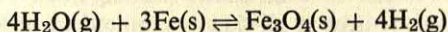
are (a) the water gas reaction, in which steam is passed over heated coke:



for which the equilibrium constant is

$$K_p = \frac{p_{\text{CO}} \times p_{\text{H}_2}}{p_{\text{H}_2\text{O}}}$$

and (b) the reaction between steam and red-hot iron, which produces hydrogen:



The equilibrium constant for the latter reaction is

$$K_p = \frac{(p_{\text{H}_2})^4}{(p_{\text{H}_2\text{O}})^4}$$

from which it follows that at any particular temperature

$$\frac{p_{\text{H}_2}}{p_{\text{H}_2\text{O}}} = \text{Constant}$$

so that the composition of the equilibrium mixture is constant and independent of the total pressure. This result could also be predicted from Le Chatelier's principle, remembering that only the *gaseous* substances present need be considered. Since the reaction causes no change in the number of gaseous molecules, the equilibrium mixture is not affected by pressure. The water gas reaction, on the other hand, produces two molecules of gas ($\text{CO} + \text{H}_2$) for every molecule of steam used up, so that an increase in the total pressure will reduce the proportion of water gas in the equilibrium mixture.

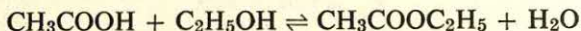
13.7. The experimental measurement of equilibrium constants

The first essential condition when studying equilibrium constants is that the system shall be left at a constant temperature until equilibrium is attained. This may take a long time if the reaction rate happens to be low, although if a suitable catalyst is available the reaction may be speeded up without affecting the final equilibrium position. Since the system must be enclosed, the reactants are usually sealed up in a suitable vessel and put into a constant-temperature bath. If the reaction involves gases, it may be necessary to measure the total pressure (this applies if there is a change in the number of gaseous molecules when the reaction takes place), and this may be done by connecting a manometer to the vessel. An alternative method, which may be used for reactions that are entirely gaseous, is to pass the reactants through a heated zone at a rate slow enough to allow equilibrium to be reached, then cool the mixture quickly so that the rate of the reaction is considerably reduced and the mixture is "frozen" at the equilibrium composition.

There are many possible ways of analysing the equilibrium mixture. They may be summarised as follows:

Chemical analysis

The actual method of analysis will depend on the chemical substances present. In the esterification reaction

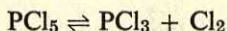


the concentration of ethanoic acid can be found by titration with alkali. If the reaction was started with known amounts of ethanoic acid and ethanol, this measurement is all that is required in order to calculate the concentrations of all four substances at equilibrium.

Physical measurements

When a solid dissociates to produce one or more gases, the equilibrium constant can be calculated from the total pressure of the system; examples were given in § 13.6. For such reactions, pressure measurements provide the best method of finding the equilibrium constant.

In the case of gaseous dissociation reactions, *e.g.*



the degree of dissociation can be calculated from a measurement of the density of the gaseous mixture (*see* p. 79), and the equilibrium constant can then be found.

Other physical properties may also be used to analyse equilibrium mixtures. They include the thermal conductivity of gases, optical rotation in the case of optically active substances in solution, and electrolytic conductivity for solutions of electrolytes. Physical properties have the advantage that they can be measured continuously while the reaction is proceeding, which makes it much easier to determine that equilibrium has been attained. When chemical methods are used, samples must be withdrawn at intervals until the analysis shows no further change in composition.

QUESTIONS

G.C.E.

1. What do you understand by the term *dynamic equilibrium*? Describe a simple experiment which would demonstrate whether a state of dynamic equilibrium exists in a selected system.

The reaction $\text{ZnO(s)} + \text{CO(g)} \rightarrow \text{Zn(g)} + \text{CO}_2\text{(g)}$ has an equilibrium constant of 1.00 atm at 1500 K. Calculate the equilibrium partial pressure of zinc vapour in a reaction vessel if an equimolar mixture of CO and CO₂ is brought into contact with solid zinc oxide at 1500 K and at a total pressure of

1.0 atm. This reaction is highly endothermic. Zinc is manufactured by bubbling the effluent gas from such a reaction vessel through molten lead at 700 K. Suggest reasons why this is done. [O. & C., "S"]

2. Write a brief account of the influence of change of pressure and temperature on the position of equilibrium of a balanced reaction, the rate at which equilibrium is attained and the value of the equilibrium constant.

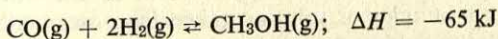
Write down equilibrium constants, K_p or K_c as appropriate, indicating their units (if any), for the following equilibrium $P + Q \rightleftharpoons 2R + S$ where, under the conditions of the experiments, (i) P , Q , R and S are all gases, (ii) P , Q , R and S are all liquids, (iii) P and S are gases, Q and R , solids.

The vapour of dinitrogen tetroxide is partially dissociated $N_2O_4 \rightleftharpoons 2NO_2$. 4.80 g of dinitrogen tetroxide occupies a volume of 1.50 dm³ at normal atmospheric pressure, 1.00×10^5 Pa (1 atmosphere) and 27°C. Calculate (i) the degree of dissociation, (ii) the equilibrium constant, K_p , at this temperature. [N = 14, O = 16, $R = 8.314 \text{ J mol}^{-1} \text{ K}^{-1}$, $J = \text{kg m}^2 \text{ s}^{-2} = \text{Nm}$, Pa = Nm⁻².] [S.U.J.B.]

3. The following equilibrium is exothermic for the left to right reaction: $2SO_2(g) + O_2(g) \rightleftharpoons 2SO_3(g)$. (a) Write down the equilibrium expression for K_c . (b) In which units will K_c be expressed? (c) Write down the equilibrium expression for K_p , explaining the symbols you use. (d) State the effect, if any, of each of the following on the equilibrium concentration of SO_3 in a particular equilibrium mixture, clearly giving the reasons: (i) decrease of pressure, (ii) decrease of temperature, (iii) addition of a catalyst, (iv) addition of an inert gas to the system at equilibrium, while maintaining the pressure constant. [W.J.E.C.]

4. Explain the effect of temperature on rate of reaction.

Methanol is manufactured by reacting carbon monoxide and hydrogen in the presence of a catalyst. The following equilibrium is attained



(a) What is the function of the catalyst? (b) Deduce the optimum conditions of temperature and pressure, explaining your reasoning. (c) Deduce an expression for K_p in terms of the total pressure of the system, P , and the number of moles of carbon monoxide, a , of hydrogen, b , and of methanol, c , present at equilibrium. In practice, if carbon monoxide and hydrogen in the molar ratio of 1:2 are used, and at equilibrium 15% of the carbon monoxide has been converted, calculate the number of moles of carbon monoxide, of hydrogen and of methanol present at equilibrium. If the equilibrium constant K_p is $4 \times 10^{-10} \text{ kPa}^{-2}$, calculate the pressure in the system. (101 kPa = 1 atm.) [A.E.B., 1976]

5. The equilibrium constant for the reaction $H_2(g) + I_2(g) \rightleftharpoons 2HI(g)$ is 60 at 450°C. The number of moles of hydrogen iodide in equilibrium with 2 mol of hydrogen and 0.3 mol of iodine at 450°C is: A $\frac{1}{100}$ B $\frac{1}{10}$ C 6 D 36 E only calculable if the volume of the container is known. [Cambridge]

CHAPTER 14

ELECTROLYTES

14.1. Electrical conduction in metals and electrolytes

Metals are good conductors of electricity because they contain a certain number of electrons which are free to move if an electric field is applied (see § 3.6). If the two ends of a piece of metal wire are connected to the terminals of a battery, the difference in potential causes electrons to flow towards the positive electrode. This movement of electrons causes a certain quantity of electricity (equal to the number of electrons travelling multiplied by the charge on an electron) to be transferred from one end of the wire to the other. This does not cause any change in the composition of the metal because the electrons that flow into the battery from one end of the wire are replaced by an equal number received from the battery at the other end.

Certain liquids can also conduct electricity; for example, if a battery is connected to two platinum electrodes immersed in a solution of copper sulphate, a current will flow. At the same time, however, it will be noticed that a deposit of metallic copper forms on the electrode connected to the negative pole of the battery, while bubbles of gas (which could be shown to be oxygen) form at the other electrode. Furthermore, if samples of solution taken from near either electrode were analysed, it would be found that the solution was no longer of the same concentration throughout. The mechanism by which electricity is conducted in the copper sulphate solution is obviously not the same as in the case of a metal. This is because copper sulphate is an electrovalent material and is therefore ionic in nature, even in the solid state. In solution, the copper and sulphate ions are free to move individually, so that when an electric field is applied the copper ions move towards the negative electrode (or *cathode*) and the sulphate ions move towards the positive electrode (or *anode*) as shown in Fig. 86. *The current is therefore carried across the solution by ions and not by electrons.* Liquids in which this type of conduction takes place are known as *electrolytes*.

When the copper ions reach the cathode they are discharged, *i.e.* they absorb electrons and become metal atoms which adhere to the electrode. At the anode, negative ions discharge and liberate electrons. Thus the flow of electrons in the external circuit is balanced by the removal of electrons from the cathode and the liberation of electrons at the anode. What is actually occurring at the electrodes is the decomposition of the electrolyte by means of the electric current, a process known as *electrolysis*. The results of electrolysis are often complicated;

for example, it is not immediately obvious why the discharge of sulphate ions should result in the liberation of oxygen as in the example given. This side of the picture will be studied in Chapter 15.

The passage of current across an electrolyte is made up of two parts: (a) carriage of positive charge towards the cathode by the positive ions (or *cations*), and (b) carriage of negative charge towards the anode by the negative ions (or *anions*). The total current is the sum of (a) and (b), since from the electrical point of view a transfer of a certain amount of

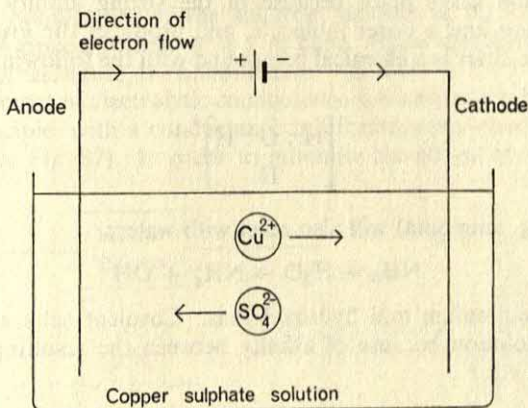


Fig. 86. Conduction in an electrolyte

positive charge in one direction is equivalent to the same amount of negative charge travelling in the opposite direction. Another result of the movement of ions in an electrolyte is that the current causes a transfer of mass, as well as of electric charge.

14.2. The nature of electrolytes

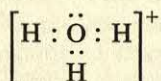
From the definition of electrolytic conductance given above, it is evident that an electrolyte must contain ions. It has been seen (§ 3.2) that electrovalent compounds consist of ions, even in the solid state. If an electrovalent substance (e.g. sodium chloride) is melted, the ions will be free to move and the liquid will therefore conduct electricity. The same will also be true for a solution of the substance. It is, in fact, found that many salts are electrolytes both in the fused state and in solution.

There are, however, other types of compound which give conducting solutions, i.e. *acids*, *bases* and *covalent salts* (e.g. Al_2Cl_6). These are all covalent substances, so that in the pure state they consist of molecules and not ions. The fact that their solutions will conduct electricity shows that the process of solution has caused *ionisation* of the molecules. Hydrogen chloride, for example, is a non-conducting liquid (when

below its boiling point) and if dissolved in dry benzene forms a non-conducting solution. When it is dissolved in water, however, the solution (hydrochloric acid) is strongly conducting and shows the usual acidic properties that we associate with the presence of hydrogen ions. This is due to ionisation, as a result of a reaction between the HCl molecule and water:



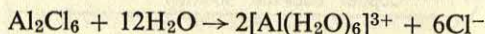
This reaction takes place because of the strong affinity between a hydrogen ion and a water molecule, and produces the *hydronium* ion H_3O^+ . The latter is a chemical compound with the following electronic structure:



A base (*e.g.* ammonia) will also react with water:



forming ammonium and hydroxyl ions. Covalent salts also tend to ionise in solution because of affinity between the resulting metal ion and water, *e.g.*:



where the water is held by dative bonds.

Ions in aqueous solution always have a certain number of water molecules attached to them, *i.e.* they are *hydrated* to a greater or lesser extent. Some of the water may be attached by chemical bonds, as in the two examples above; in addition, some will be held by electrostatic attraction between the charged ions and the polar water molecules (*see* Fig. 48). When the chemical formula of an ion is written, the attached water is sometimes shown, but more often omitted: thus the hydrogen ion in aqueous solution is alternatively written as H^+ or H_3O^+ . It must be remembered that the latter is correct, the former being an abbreviated way of writing it. In the same way the aluminium ion is usually shown as Al^{3+} whereas it actually exists in the hydrated form shown above.

The above reactions, whereby a solvent causes ionisation of the dissolved material, are all reversible, and the extent to which ionisation occurs varies very widely according to the nature of both the dissolved material and the solvent. If a substance is completely (or almost completely) ionised in solution, it is known as a *strong electrolyte*. Hydrochloric acid is one example, and solutions of all electrovalent salts are strong electrolytes, since the latter are completely ionised even before they are dissolved. On the other hand, many acids and bases show very little ionisation in solution, and are classed as *weak electrolytes*. Since

ionisation involves a reaction between solute and solvent, the extent to which any particular compound is ionised will depend on the solvent used: a substance which is a strong electrolyte in one solvent may become a weak electrolyte in a different solvent. In this book, however, only solutions in water will be considered.

14.3. The conductance of electrolytes: molar conductivity

Much useful information about electrolytes can be obtained by studying their electrical conductance. This is measured in terms of the *electrolytic conductivity* of the solution, defined as the conductance between the opposite faces of a 1 m cube. Since conductance is the reciprocal of resistance, the units are S m^{-1} ($\text{S} = \Omega^{-1}$).

Measurement of electrolytic conductance is based on the Wheatstone bridge principle, with a conductance cell forming the unknown resistance R_4 (see Fig. 87). In order to minimise the effects of electrolysis,

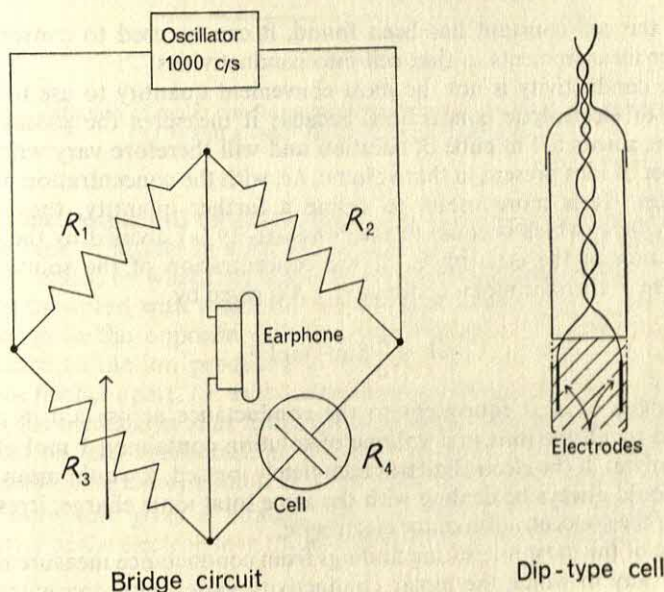


Fig. 87. Bridge circuit for measuring electrolytic conductance

the bridge is operated with alternating current (1000 Hz or more), so that the direction of flow alternates very rapidly. The effects produced during the short time that the current is flowing in one direction through the cell (*i.e.* changes in concentration, and liberation of substances at the electrodes) are small, and are counteracted when the current reverses its direction. For approximate work, the balance point may be found by using a telephone receiver, and adjusting the value of

R_3 until the minimum sound is heard (owing to the capacitance of the cell, the bridge cannot be exactly balanced in the form shown). More accurate bridges use an amplifier and provide a means of balancing out the capacitance of the cell.

The conductance cell consists essentially of two platinum electrodes fixed rigidly in a glass vessel. The dip-type cell shown in Fig. 87 is very useful for work of moderate accuracy.

The actual bridge measurement gives the value of R_4 , the resistance of the cell when filled with a particular solution: the conductance is therefore $1/R_4$. It is not possible to calculate the conductivity from the cell dimensions, because the path of the current through the solution is uncertain. Instead, the cell is filled with a solution of known conductivity and the resistance of the cell measured; the *cell constant* is then calculated from the equation:

$$\text{Conductivity} = \text{Measured conductance of cell} \times \text{Cell constant}$$

Once the cell constant has been found, it can be used to convert all further measurements in that cell into conductivities.

The conductivity is not the most convenient quantity to use for the study of electrolytic conduction, because it measures the passage of current across a 1 m cube of solution and will therefore vary with the number of ions present in that volume, *i.e.* with the concentration of the solution. It is more useful to define a further quantity, the *molar conductivity*, which is equal to the conductivity (κ) divided by the concentration of the electrolyte. If the concentration of the solution is c mol m⁻³, then the molar conductivity Λ is given by

$$\Lambda = \frac{\kappa}{c} \text{ S m}^2 \text{ mol}^{-1}$$

The value of Λ is equivalent to the conductance across a 1 m path, caused by all the ions in a volume of solution containing 1 mol of the electrolyte. If the electrolyte was completely ionised, it would mean that we should always be dealing with the same total ionic charge, irrespective of the concentration of the electrolyte.

One of the most interesting findings from conductance measurements is the way in which the molar conductivity varies with concentration (Fig. 88). For a weak electrolyte (*e.g.* ethanoic acid) the value of Λ falls off very rapidly with increasing concentration, showing that the extent of ionisation is decreasing. At moderate concentrations Λ is so small that the number of ions present cannot be more than a small fraction of the number of ethanoic acid molecules present.

A strong electrolyte (*e.g.* KCl) shows a small drop in Λ as the concentration increases. Since the KCl is completely ionised and Λ measures the conductance due to a constant number of ions, it might be expected that there would be no change with concentration. Debye

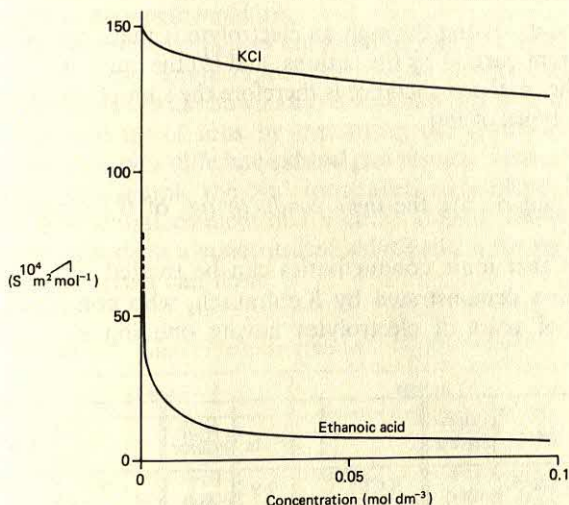


Fig. 88. Variation of molar conductance with concentration for a strong electrolyte (KCl) and a weak electrolyte (ethanoic acid).

and Hückel explained the actual behaviour by supposing that each ion would tend to attract to itself ions of the opposite sign, and so would be surrounded by what they called an “ionic atmosphere”, which could reduce the speed with which the ion travelled by exerting an electrical attraction in the opposite direction (see Fig. 89). The extent of the resistance to motion produced in this way will decrease as the ions become farther apart, *i.e.* as the concentration of the solution decreases, hence the increase in Λ at lower concentrations. If the graph is extrapolated to zero concentration, the *limiting molar conductivity* (Λ_0) is obtained. The extrapolation is more accurate if Λ is plotted against $\sqrt{c}$, since this gives a straight line. Λ_0 represents the molar conductivity of the electrolyte in the absence of any ionic atmosphere effect.

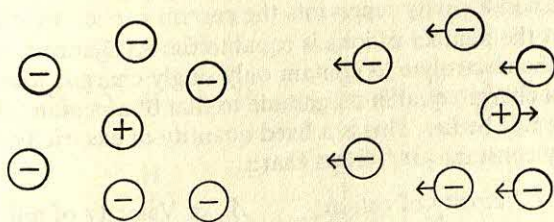


Fig. 89. Ionic atmosphere effect

14.4. Ionic conductivities

The current passing through an electrolyte is made up of two parts: (a) the current carried by the cations, and (b) the current carried by the anions. The total conductance is therefore the sum of the conductances of the two types of ion:

$$\Lambda_0 = \Lambda_+ + \Lambda_-$$

where Λ_+ and Λ_- are the *ionic conductivities* of the cation and anion respectively.

The fact that ionic conductivities can be treated separately in this way was first demonstrated by Kohlrausch, who compared the conductances of pairs of electrolytes having one ion in common, for example:

	$10^4 \Lambda_0$	Diff- erence		$10^4 \Lambda_0$	Diff- erence		$10^4 \Lambda_0$	Diff- erence
NaCl	126.5	4.9	KCl	149.9	4.9	HCl	426.2	4.9
NaNO ₃	121.6		KNO ₃	145.0		HNO ₃	421.3	

For the first pair, we can write:

$$\Lambda_0(\text{NaCl}) = \Lambda_+(\text{Na}^+) + \Lambda_-(\text{Cl}^-)$$

$$\Lambda_0(\text{NaNO}_3) = \Lambda_+(\text{Na}^+) + \Lambda_-(\text{NO}_3^-)$$

If the second equation is subtracted from the first, this gives:

$$\Lambda_0(\text{NaCl}) - \Lambda_0(\text{NaNO}_3) = \Lambda_-(\text{Cl}^-) - \Lambda_-(\text{NO}_3^-)$$

The right-hand side of this equation will be the same for all three pairs of salts, so that if this reasoning is correct the difference in conductivity should be the same in each case, as indeed it is.

The ionic conductivity can also be related to the speed at which the ions travel. The current carried by an ion will depend on the rate at which it conveys electrical charge across the solution, *i.e.*

$$\text{Total current} \propto \text{Number of ions} \times \text{Charge} \times \text{Velocity}$$

The ionic conductivity represents the current carried by one mole of ions, so that the number of ions is equal to the Avogadro constant (L). Supposing the electrolyte to contain only singly charged ions, *i.e.* each ion carries a charge equal in magnitude to that of a proton (e), then the total charge will be Le . This is a fixed quantity of electricity, known as the Faraday constant. It follows that:

$$\Lambda_+ \propto \text{Velocity of cation} \quad \Lambda_- \propto \text{Velocity of anion}$$

The velocities given in this relationship are actually equal to the speed

at which the ions move when there is a potential gradient of 1 V m^{-1} : this is known as the *ionic mobility*.

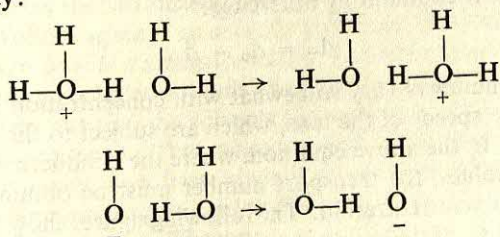
Some ionic conductivity figures are given in Table 7. They have been obtained partly from conductance measurements, which can be used to find difference values as shown above, and partly from determination of the actual velocity of ions by measuring the speed at which the boundary between two different electrolytes moves. Ions do not move very rapidly, for example the Na^+ ion travels only about 2 cm in an hour under a potential gradient of 1 V cm^{-1} ; there is, however, a very large number of ions in a concentrated solution of a strong electrolyte, so that a large current can flow.

TABLE 7. IONIC CONDUCTIVITIES AT 25°C ($\text{S m}^2 \text{ mol}^{-1}$)

Cations		Anions	
H^+	0.0350	OH^-	0.0199
Na^+	0.0050	Cl^-	0.0076
K^+	0.0074	NO_3^-	0.0072
Ag^+	0.0062	HCOO^-	0.0045

Comparison of ionic conductivity figures can throw some light on the extent to which ions in solution are hydrated. All the ions given in Table 7 have a single charge, so that the force acting on each ion due to a unit potential gradient will be the same. Assuming that the ions are all spherical in shape, the speed of an ion will depend on its size: a small ion will travel faster than a large one. Now Na^+ is smaller than K^+ as far as the actual ions themselves are concerned, but the figures show that Na^+ in solution has a lower conductivity than that of the K^+ , so that the sodium ion *when in solution* must be larger than the potassium ion. This is because the former attracts more water molecules, *i.e.* it is hydrated to a greater extent, than the latter.

The conductivity figures also show that hydrogen and hydroxyl ions conduct electricity at a much higher rate than other ions—too high, in fact, to be accounted for by the movement of the ions themselves. It is thought that the H_3O^+ and OH^- ions are able to pass on their charge to an adjoining water molecule by the transfer of a proton (H^+), in the following way:



This process can be continued through the electrolyte, and causes the charge to travel faster through the solution than the speed at which the ions can move.

14.5. Transport numbers

Different types of ion move at different speeds under the same potential gradient. It follows that the cations and anions in an electrolyte will carry different amounts of electricity. The fraction of the total current carried by either ion is known as the *transport number*. Since the current carried by an ion is proportional to its ionic conductivity, we have

$$\text{Current carried by cation} \propto \Lambda_+$$

$$\text{Current carried by anion} \propto \Lambda_-$$

$$\text{Total current} \propto (\Lambda_+ + \Lambda_-)$$

$$\text{Transport number of cation } t_+ = \frac{\Lambda_+}{\Lambda_+ + \Lambda_-}$$

$$\text{Transport number of anion } t_- = \frac{\Lambda_-}{\Lambda_+ + \Lambda_-}$$

hence

$$t_+ + t_- = 1$$

Transport numbers can be connected with the changes in concentration that take place near the two electrodes when a current is passed through an electrolyte, and this is the basis of one method for determining their value (see § 15.7).

An important application of transport numbers is in the determination of ionic conductivities. For the cation in an electrolyte, for example, we have

$$t_+ = \frac{\Lambda_+}{\Lambda_+ + \Lambda_-}$$

$$\Lambda_+ = t_+(\Lambda_+ + \Lambda_-)$$

$$= t_+\Lambda_0$$

In the case of a strong electrolyte the value of Λ_0 can be found from conductance measurements, so Λ_+ can be found if t_+ is known. The value of Λ_- is then found by difference:

$$\Lambda_- = \Lambda_0 - \Lambda_+$$

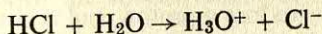
Transport numbers vary somewhat with concentration because they depend on the speeds of the ions, which are subject to the ionic atmospheric effect. In the above equation, where the conductivity figures are the limiting values, the transport number must be obtained by extrapolation to zero concentration. The following figures show the transport number, at 25°C, of the cation in various electrolytes. It is not necessary

to state the value for the anion, since it can be obtained by subtracting the cation transport number from unity ($t_- = 1 - t_+$).

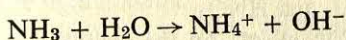
<i>Electrolyte</i>	HCl	NaCl	KCl	KNO ₃	NaOH
t_+	0.821	0.395	0.491	0.507	0.290

14.6. Acids and bases

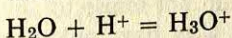
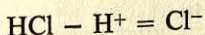
It is usual to associate *acidic* properties in a solution with certain characteristic reactions, such as altering the colour of an indicator (*e.g.* turning blue litmus red), neutralising a base, or reacting with certain metals with the evolution of hydrogen. These properties all result from the presence of hydrogen ions produced by a reaction between the acid and the solvent, as for example when hydrochloric acid is produced by dissolving hydrogen chloride in water:



Similarly, a solution showing *basic* properties will also affect the colour of indicators (*e.g.* red litmus turned blue), will neutralise an acid, and precipitate certain metals as hydroxides. In this case the properties are due to hydroxyl ions, again the result of reaction between the base and the solvent. The basic nature of ammonia solution, for example, is caused by a small proportion of the ammonia molecules reacting with water in the following way:

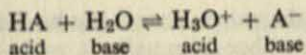


The above reactions have one point in common: they both involve the transfer of a proton (H^+) from one molecule to another. In the case of an acid (*e.g.* HCl), the acid molecule loses a proton by transferring it to the water molecule:

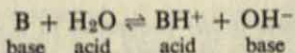


In the case of a base, the water loses the proton ($\text{H}_2\text{O} \rightarrow \text{OH}^- + \text{H}^+$), and it is acquired by the base. Another property of acids and bases is that they are able to catalyse certain reactions, and it was mainly as a result of a study of the types of ions (or molecules) that could cause this kind of catalysis that Brønsted and Lowry, in 1923, defined acids and bases in the following way: *an acid is a substance with a tendency to lose a proton, and a base is a substance with a tendency to gain a proton.*

This definition includes not only the substances that we normally call acids and bases but also the solvents that cause them to ionise and the ions that are produced. Thus when an acid is dissolved in water, the water itself is acting as a base, since it accepts the proton that is lost by the acid. Representing an acid as HA, a solution of the acid in water contains the following equilibrium:

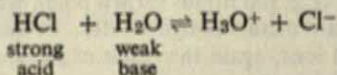


In the reverse reaction, the hydrogen ion loses a proton, and is therefore an acid; while the A^- ion, which gains a proton, is a base. The ionisation of an acid or base always contains this equilibrium between two pairs of acids and bases. For a base (B) dissolved in water, the equilibrium is:



It will be noticed that water has the property of being able to act either as an acid or a base.

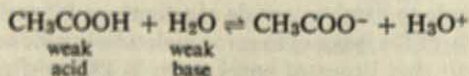
The extent to which acids or bases are ionised by these reactions depends on the relative ease with which, for example, an acid can lose a proton and the solvent molecule can gain it. Hydrochloric acid has a very strong tendency to lose a proton, and is therefore referred to as a *strong acid*: although water is only a weak base (*i.e.* has only a weak tendency to gain a proton), the reaction



results in virtually complete ionisation of the acid, *i.e.* the equilibrium mixture contains hardly any HCl molecules. Other examples of strong acids are HBr, H_2SO_4 and HNO_3 .

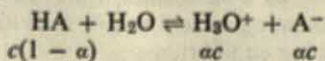
The influence of the solvent on the equilibrium is very important: in a solvent which is an even weaker base than water (*e.g.* ethanoic acid) the tendency for the proton transfer to occur is less, and acids that are completely ionised in aqueous solution will only be ionised to a small extent. In this way it is possible to find the relative strengths of the strong acids mentioned above.

The majority of acids do not ionise to any large extent in aqueous solution, in other words they have only a small tendency to lose a proton and are therefore *weak acids*. In a solution of ethanoic acid, for example, where we have the equilibrium



the proportion of ethanoic acid that is ionised in a 0.1 mol dm^{-3} solution at 25°C is only 1.3% .

The extent of ionisation of a weak acid can be expressed either in terms of the equilibrium constant for the reaction, or as the degree of ionisation. For a weak acid HA dissolved in water



if α is the proportion of HA that has reacted, then α is known as the *degree of dissociation* or the *degree of ionisation*. If the initial concentration of HA was c , then the concentration of each of the ions formed is αc , and the concentration of unchanged acid is $c(1 - \alpha)$. The equilibrium constant for the reaction is

$$K_a = \frac{[\text{H}_3\text{O}^+][\text{A}^-]}{[\text{HA}]}$$

where K_a is the *dissociation constant* (or *ionisation constant*) of the acid. If the solution is not too concentrated, the concentration of water molecules is very nearly constant and equal to the concentration in pure water; by convention the latter is taken as equal to unity, so that the concentration of the water does not appear in the equilibrium constant expression. This may be compared with the convention already adopted in dealing with the concentration terms for pure solids in heterogeneous equilibria (§ 13.6).

When dealing with aqueous solutions, the hydrated hydrogen ion (H_3O^+) is usually referred to simply as the "hydrogen ion" (H^+), and the acid dissociation constant is written

$$K_a = \frac{[\text{H}^+][\text{A}^-]}{[\text{HA}]}$$

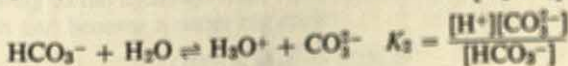
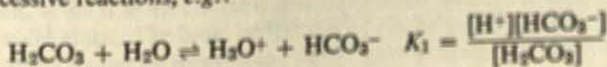
but it must be understood that the symbol H^+ refers to the ion as it exists in solution as the hydrated ion.

The dissociation constant is the most convenient measure of the strength of an acid: the smaller the value of K_a , the weaker the acid. The dissociation constants of some common acids are given in Table 8.

TABLE 8. DISSOCIATION CONSTANTS OF ACIDS AND BASES AT 25°C

Acids	K_a	Bases	K_b
methanoic acid	1.77×10^{-4}	ammonia	1.74×10^{-5}
ethanoic acid	1.75×10^{-5}	methylamine	5.01×10^{-4}
phenol	1.20×10^{-10}	phenylamine	4.07×10^{-10}
carbonic acid	(1) 4.47×10^{-7} (2) 5.62×10^{-11}		
hydrogen sulphide	(1) 1.0×10^{-7} (2) 1.2×10^{-13}		
hydrogen cyanide	4.8×10^{-10}		

It will be noticed that two figures are given for carbonic acid and for hydrogen sulphide. The reason is that these acids can lose two protons in successive reactions, e.g.:



The dissociation constant for the second stage of ionisation (K_2) is always less than K_1 , because it is more difficult to remove a proton from the negatively charged ion (*e.g.* HCO_3^-) produced in the first stage.

The degree of dissociation α can be found by substituting the following concentrations in the dissociation constant expression:

$$[\text{H}^+] = [\text{A}^-] = \alpha c \quad [\text{HA}] = c(1 - \alpha)$$

$$K_a = \frac{[\text{H}^+][\text{A}^-]}{[\text{HA}]}$$

$$= \frac{\alpha c \times \alpha c}{c(1 - \alpha)}$$

$$= \frac{\alpha^2 c}{1 - \alpha}$$

As K_a is an equilibrium constant it will vary with temperature, but at any particular temperature it will have a fixed value. The degree of dissociation, on the other hand, will vary with the concentration of the solution in accordance with the above equation, as will be seen from the following figures for ethanoic acid solutions:

$c \text{ (mol dm}^{-3}\text{)}$	0.1	0.01	0.001	0.0001
α	0.013	0.041	0.124	0.340

At moderate concentrations, a weak acid like ethanoic acid is ionised to only a small extent; an acid with an even smaller dissociation constant will show correspondingly less ionisation (*e.g.* for a 0.1 mol dm^{-3} solution of HCN, $\alpha = 0.000085$). On the other hand, as the concentration is reduced the degree of ionisation increases, and at an extremely low concentration all acids would be completely ionised. This explains the type of curve obtained for the molar conductivity of a weak electrolyte (Fig. 88): if measurements could be made at sufficiently low concentrations, the conductivity would approach the value for the completely ionised electrolyte. For ethanoic acid, for example, the molar conductivity at zero concentration would be

$$\Lambda_0 = \Lambda_{\text{CH}_3\text{COO}^-} + \Lambda_{\text{H}^+}$$

The molar conductivity (Λ) of an actual solution will be less than Λ_0 , since only a proportion α of the electrolyte is ionised. The actual relationship will be

$$\Lambda = \alpha \Lambda_0$$

or

$$\alpha = \frac{\Lambda}{\Lambda_0}$$

This provides a method for measuring the dissociation constant of a weak acid. Λ is found by measuring the conductance of a solution containing a known concentration of the acid. The value of Λ_0 cannot be found by direct measurement, but must be obtained from the sum of the ionic conductivities: for example, in the case of an acid HA,

$$\Lambda_0(\text{HA}) = \Lambda_{\text{H}^+} + \Lambda_{\text{A}^-}$$

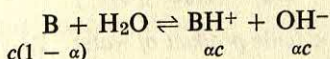
The value of Λ_{H^+} can be found from tables, but Λ_{A^-} may have to be determined separately from conductance measurements on a salt of the acid, e.g. NaA, which will be a strong electrolyte:

$$\Lambda_0(\text{NaA}) = \Lambda_{\text{Na}^+} + \Lambda_{\text{A}^-}$$

Since Λ_{Na^+} is known, measurement of Λ_0 therefore gives Λ_{A^-} .

The extent to which a base ionises in solution is determined by the relative strength of the base itself and also that of the solvent (acting as an acid). Ammonia, for example, is a weak base, while water acts as a very weak acid. In a solution of ammonia, therefore, the tendency for proton transfer between base and solvent is not large, and only a small proportion of the ammonia molecules are ionised.

The ionisation equilibrium for a base can be written:



where B represents any base and the concentrations are shown in terms of the degree of dissociation α . The equilibrium constant for this reaction, *i.e.* the dissociation constant of the base, is:

$$K_b = \frac{[\text{BH}^+][\text{OH}^-]}{[\text{B}]}$$

the concentration of water molecules being taken as unity for the reasons already given. Substituting for the concentrations in terms of the degree of dissociation,

$$K_b = \frac{\alpha^2 c}{1 - \alpha}$$

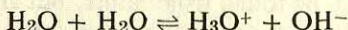
One method of determining the dissociation constant of a base is by conductance measurements, the relation between α and the conductance being the same as for solutions of weak acids. The dissociation constants of some bases are given in Table 8.

The so-called strong base, caustic soda, is more accurately described as a salt, since it is an electrovalent compound and completely ionised in the solid state. The basic properties of a solution of caustic soda are due entirely to the hydroxyl ions, which have a strong tendency to gain a proton and become a water molecule:



14.7. The ionisation of water

Water is a very weak conductor of electricity, which shows that it is ionised to a very small extent. It has already been seen that water, when acting as a solvent for acids or bases, can act either as a weak base or a weak acid. It is therefore possible for two water molecules to exchange a proton, one molecule losing the proton (acid behaviour) and the other gaining it (basic behaviour):



The tendency for the transfer to occur is low, and the equilibrium constant for the reaction,

$$K = \frac{[\text{H}_3\text{O}^+][\text{OH}^-]}{[\text{H}_2\text{O}]^2}$$

will therefore be a very small figure. Since the ionic concentrations are small, the concentration of H_2O molecules may be taken as constant and equal to unity, by the convention employed previously. The equilibrium constant then becomes equal to the product of the ionic concentrations

$$K_w = [\text{H}_3\text{O}^+][\text{OH}^-]$$

and K_w is known as the *ionic product of water*. Its value, which can be determined by measuring the conductance of pure water, is 1.01×10^{-14} at 25°C and increases fairly rapidly with increasing temperature.

The value of K_w is extremely important, since in aqueous solutions the concentrations of the hydrogen and hydroxyl ions are always related in this way.

14.8. Hydrogen ion concentration: the pH scale

When a strong acid is dissolved in water, it is completely dissociated into ions, so that the concentration of hydrogen ions is equal to the concentration of acid dissolved. Thus in a 0.1 mol dm^{-3} solution of an acid, $[\text{H}^+] = 0.1$. If the acid is weak, then $[\text{H}^+] = \alpha c$ (see p. 230): the weaker the acid, the smaller the value of $[\text{H}^+]$ for a given concentration of the acid. We can also express $[\text{H}^+]$ in terms of the dissociation constant of the acid:

$$K_a = \frac{\alpha^2 c}{1 - \alpha}$$

and for a weak acid, in not too dilute a solution, α is small compared with unity, so that it is approximately correct to write

$$K_a = \alpha^2 c$$

$$\alpha = \sqrt{\frac{K_a}{c}}$$

hence

$$[\text{H}^+] = \alpha c = \sqrt{K_a c}$$

When a base is dissolved in water, hydroxyl ions are produced. In a solution of a strong base, the concentration of hydroxyl ions will be equal to the concentration of the base. For a weak base, $[\text{OH}^-] = \alpha c$ and α is related to the dissociation constant of the base by the equation:

$$K_b = \alpha^2 c$$

so that

$$[\text{OH}^-] = \sqrt{K_b c}$$

The hydrogen ion concentration can be found by combining this with the ionic product of water:

$$K_w = [\text{H}^+][\text{OH}^-]$$

$$\begin{aligned} [\text{H}^+] &= \frac{K_w}{[\text{OH}^-]} \\ &= \frac{K_w}{\sqrt{K_b c}} \end{aligned}$$

In pure water the concentrations of hydrogen and hydroxyl ions must be equal, so that

$$[\text{H}^+] = [\text{OH}^-] = \sqrt{K_w}$$

and at 25°C K_w is almost exactly equal to 10^{-14} . Hence

$$\begin{aligned} [\text{H}^+] &= \sqrt{10^{-14}} \\ &= 10^{-7} \end{aligned}$$

In an acid solution, the hydrogen ion concentration will be greater than 10^{-7} . In a basic solution the hydroxyl ion concentration is greater than in pure water, so that $[\text{H}^+]$ will be less than 10^{-7} . We can therefore regard $[\text{H}^+] = 10^{-7}$ as the *neutral point* for aqueous solutions.

Since hydrogen ion concentrations vary widely in solutions of acids and bases, and are nearly always less than unity, it is more convenient to use a logarithmic scale defined in the following way:

$$\text{pH} = -\log_{10}[\text{H}^+]$$

i.e. the pH of a solution is the negative logarithm of the hydrogen ion concentration. The neutral point will be:

$$\begin{aligned} \text{pH} &= -\log_{10} 10^{-7} \\ &= 7 \end{aligned}$$

If $[\text{H}^+]$ is greater than that of pure water (*i.e.* the solution is acid), then the negative logarithm of $[\text{H}^+]$ will be smaller than 7; in a basic or

alkaline solution $[H^+]$ will be less than 10^{-7} and the pH will be greater than 7. The range of pH values normally encountered will be seen from the following example.

EXAMPLE

Calculate the pH of 0.1 mol dm^{-3} solutions of the following: (a) hydrochloric acid, (b) ethanoic acid, (c) ammonia, (d) sodium hydroxide.

(a) Since hydrochloric acid is a strong acid:

$$\begin{aligned}[H^+] &= 0.1 \\ \text{pH} &= -\log_{10} 0.1 \\ &= 1\end{aligned}$$

(b) K_a for ethanoic acid (Table 8) is 1.75×10^{-5} .

$$\begin{aligned}[H^+] &= \sqrt{K_a c} \\ &= \sqrt{1.75 \times 10^{-5} \times 0.1} \\ &= 1.32 \times 10^{-3} \\ \text{pH} &= -(3.12) \\ &= 2.88\end{aligned}$$

(c) K_b for ammonia is 1.74×10^{-5} :

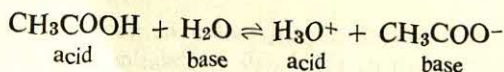
$$\begin{aligned}[H^+] &= \sqrt{\frac{K_w}{K_b c}} \\ &= \frac{10^{-14}}{\sqrt{1.74 \times 10^{-5} \times 0.1}} \\ &= 7.58 \times 10^{-12} \\ \text{pH} &= -12.88 \\ &= 11.12\end{aligned}$$

(d) Sodium hydroxide is completely ionised, so that $[OH^-] = 0.1$:

$$\begin{aligned}[H^+] &= \frac{K_w}{[OH^-]} \\ &= \frac{10^{-14}}{0.1} \\ &= 10^{-13} \\ \text{pH} &= 13\end{aligned}$$

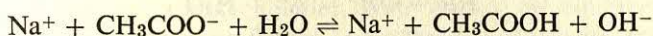
14.9. Hydrolysis of salts

When a weak acid (e.g. ethanoic acid) is dissolved in water, there is the following equilibrium:



The reverse reaction, like the forward reaction, results in a proton transfer: the hydrogen ion loses a proton (and is therefore an acid), while the ethanoate ion gains the proton and is therefore a base. Ethanoic acid is a weak acid, so that the molecule CH_3COOH does not show any great tendency to lose a proton. It follows that the ethanoate ion CH_3COO^- must have a much greater tendency to gain a proton, *i.e.* it is a fairly strong base. Exactly the same considerations apply to the H_2O and H_3O^+ : the former is a weak base, so that the latter is a strong acid. These are examples of *conjugate pairs* of acids and bases. In such pairs, if one partner is weak the other must be strong.

If sodium ethanoate is dissolved in water, the ethanoate ions show the normal behaviour of a base, *i.e.* they take part in a proton transfer reaction with the water:

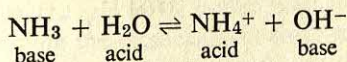


The sodium ions take no part in this equilibrium, so that they can be omitted, leaving:

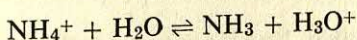


The result of this reaction is to increase the concentration of hydroxyl ions, so that the solution is alkaline. This type of reaction is known as *hydrolysis* of the salt, and the extent to which it takes place depends on how strong a base the anion (in this case the ethanoate ion) is. This in turn depends on how weak was the conjugate acid, *i.e.* the acid from which the salt was made. The salt of a weak acid always gives an alkaline solution, and the weaker the acid the more alkaline is the solution. For example, a 0.1 mol dm^{-3} solution of sodium ethanoate (K_a for ethanoic acid is 1.75×10^{-5}) has a pH of 8.9 whereas for sodium cyanide (HCN being a much weaker acid, with $K_a = 4.8 \times 10^{-10}$) the pH would be 11.2.

A salt of a weak base and a strong acid (*e.g.* ammonium chloride) is subject to hydrolysis because the ion conjugate to the weak base is a fairly strong acid. This can be seen from the ionisation reaction of a weak base (*e.g.* ammonia):



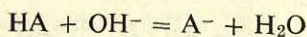
In a solution of ammonium chloride, the NH_4^+ ion reacts as an acid:



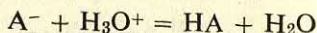
The hydrogen ions produced make the solution acid, and again the acidity depends on the relative weakness of the base from which the salt is made. A 0.1 mol dm^{-3} solution of ammonium chloride has a pH of 5.1, while a salt of a weaker base would give a more acid solution (*i.e.* smaller pH).

14.10. Buffer solutions

It is frequently necessary to make up solutions of known pH which will be capable of maintaining a nearly constant pH value even though small amounts of acid or alkali are added. Solutions of strong acids or bases are unsuitable for this purpose; for example, a solution of pH 5 could be prepared by diluting hydrochloric acid solution to $0.00001 \text{ mol dm}^{-3}$, but minute amounts of either acid or alkali would cause a considerable change in pH. To resist change in pH, a solution must contain a reasonable concentration of both an acid and a base, and this can be achieved by dissolving both a weak acid and its salt in the same solution. The weak acid (HA) can react with a base, so that if hydroxyl ions are added to the solution the following reaction occurs:



while the salt provides the ion A^- , which is conjugate to the weak acid and is therefore a base and capable of reacting with added acid (H_3O^+):



Both of these reactions go virtually to completion, because the reverse reaction has very little tendency to take place, water being very weak both as an acid and as a base. The result is that the solution can resist pH change by removing both acids and bases (in reasonable amounts) that are added to the solution. Such a solution is known as a *buffer solution*.

While a buffer solution can *resist* pH change, it cannot eliminate it entirely. The pH of the solution depends on the relative concentrations of the weak acid and the salt, and this ratio is altered when acids or bases are added. If, however, the concentration of the buffer solution is considerably greater than the concentration of any added acid or base, the change in pH will be small.

The pH of a buffer solution can be calculated from the dissociation constant of the weak acid:

$$K_a = \frac{[\text{H}^+][\text{A}^-]}{[\text{HA}]}$$

or

$$[\text{H}^+] = K_a \frac{[\text{HA}]}{[\text{A}^-]}$$

The salt of the acid (e.g. NaA) is entirely in the form of ions, and the high concentration of A^- ions supplied in this way reduces still further the ionisation of the weak acid, so that it can be assumed that all the A^- ions have come from the salt, i.e. $[\text{A}^-] = [\text{salt}]$. For the same reason, the concentration of HA molecules can be taken as the concentration of the acid in the solution, i.e. $[\text{HA}] = [\text{acid}]$.

Hence

$$[\text{H}^+] = K_a \frac{[\text{acid}]}{[\text{salt}]}$$

or

$$\text{pH} = -\log_{10} K_a + \log_{10} \frac{[\text{salt}]}{[\text{acid}]}$$

For the buffer action to be effective, it is desirable that there should be a reasonable concentration of both acid and salt present, so that the ratio $[\text{salt}]/[\text{acid}]$ can only be varied within the limits of about 10/1 to 1/10, giving a *useful range* for any particular acid of approximately

$$\text{pH} = -\log_{10} K_a \pm 1$$

Within this range, a buffer solution of any desired pH can be made by choosing the correct ratio for the concentrations of salt and acid. The most convenient way of preparing buffer solutions is to take a solution of the acid (of known strength) and add the correct amount of a standard solution of a strong base: the amount of salt formed is equivalent to the amount of base added, and the amount of acid left is obtained by difference.

EXAMPLE

To 100 cm³ of a 0.1 mol dm⁻³ solution of ethanoic acid is added 30 cm³ of 0.1 mol dm⁻³ sodium hydroxide solution. What is the pH of the buffer solution produced?

The quantity of salt formed is equivalent to 30 cm³ of 0.1 mol dm⁻³ solution. The acid left is equivalent to 100 - 30 = 70 cm³ of 0.1 mol dm⁻³ solution. K_a for ethanoic acid is 1.75×10^{-5} :

$$\begin{aligned} \text{pH} &= -\log_{10} K_a + \log_{10} \frac{[\text{salt}]}{[\text{acid}]} \\ &= -\log_{10} (1.75 \times 10^{-5}) + \log_{10} \frac{30}{70} \\ &= -(5.24) + 1.63 \\ &= -(-4.76) - 0.37 \\ &= 4.39 \end{aligned}$$

The equation for the pH of a buffer solution provides a further method for determining the dissociation constant of a weak acid. The simplest way of proceeding is to take equal amounts (in moles) of the acid and salt, so that $[\text{salt}] = [\text{acid}]$. Then

$$\log_{10} \frac{[\text{salt}]}{[\text{acid}]} = 0$$

so that

$$\text{pH} = -\log_{10} K_a$$

and if the pH of the solution is measured, the value of K_a is easily calculated.

14.11. Indicators

Substances whose colour, when in solution, depends on the hydrogen ion concentration are known as *acid-base indicators*. They are weak organic acids or bases, and the colour change is due to there being two alternative structural forms: the two forms may have different colours (e.g. methyl orange), or one form may be coloured and the other colourless, as in the case of phenolphthalein (see Fig. 90).

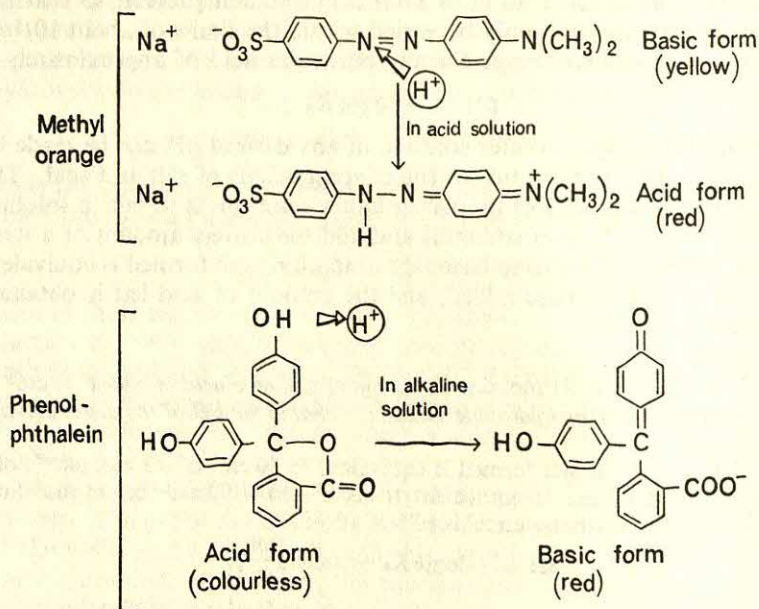
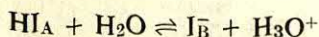


Fig. 90. Structural changes in indicator molecules due to basic behaviour (methyl orange) and acidic behaviour (phenolphthalein)

Suppose an indicator molecule (of the acid type) is represented by HI_A . When dissolved in water it will react with the solvent and ionise in the usual way, but the I_A^- ion that is formed changes into the other structural form, i.e. it becomes I_B^- . A and B represent the two different forms, and therefore the two colours of the indicator. The ionisation reaction can therefore be written:



The equilibrium constant for this reaction is called the *indicator constant* (K_I):

$$K_\text{I} = \frac{[\text{I}_\text{B}^-][\text{H}_3\text{O}^+]}{[\text{HI}_\text{A}]}$$

Writing the hydrogen ion as H^+ , this gives:

$$[H^+] = K_I \frac{[HI_A]}{[I_B]}$$

If the hydrogen ion concentration of the solution is altered, e.g. by adding an acid or a base, the ratio $[HI_A]/[I_B]$ will alter, and since HI_A and I_B have different colours this will alter the colour of the solution. Visible colour changes will only be produced over a small range of hydrogen ion concentrations, because it is impossible to detect by eye a small amount of one colour mixed with a large amount of another. Taking negative logarithms of the above equation, we have

$$pH = -\log_{10} K_I - \log_{10} \frac{[\text{colour A}]}{[\text{colour B}]}$$

and the useful range of an indicator corresponds approximately with a ratio of 1/10 and 10/1 for the proportions of the two colours. This gives the *indicator range* as approximately $-\log_{10} K_I \pm 1$. Details of colours and ranges of the more commonly used indicators are given in Table 9.

TABLE 9. ACID-BASE INDICATORS

Indicator	Colour		$-\log_{10} K_I$	pH range
	Acid	Alkaline		
methyl orange	red	yellow	3.7	3.1-4.4
methyl red	red	yellow	5.1	4.2-6.3
litmus	red	blue		5.0-8.0
phenolphthalein	colourless	red	9.4	8.3-10.0

Within its particular range, the colour of an indicator changes gradually as the pH is altered. Thus methyl orange is yellow in a solution of pH 4.4; if the acidity of the solution is increased slowly, the colour will change through various shades of orange until at pH 3.1 it has reached the red (acid) colour, and beyond this point no further change will be observed. The pH of a solution within the range 3.1-4.4 can be measured by matching the colour obtained when methyl orange is added, with solutions of known pH to which the same concentration of indicator has been added. Buffer solutions, varying in steps of 0.2 of a pH unit, are used for this purpose.

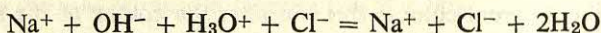
A large number of different indicators are available, covering between them the whole of the pH range. It is also possible to mix some of these indicators to give a wider range: the BDH Universal Indicator (containing five different indicators) covers the range pH 4 to 11.

Indicators are mainly used in titrations, where an indication of pH to within a few units is normally sufficient, and for other purposes where high accuracy is not required. Accurate pH determinations are

based on electrical measurement, *e.g.* using the pH meter with a glass electrode.

14.12. Neutralisation

When solutions of a strong base (*e.g.* NaOH) and a strong acid (*e.g.* HCl) are mixed, the following reaction takes place:



the products being a salt (NaCl) and water. It will be seen, however, that the Na^+ and Cl^- ions do not take any actual part in the reaction, which is simply a proton transfer from the strong acid H_3O^+ to the strong base OH^- . If equivalent amounts of acid and base are used, the result will be a solution of NaCl in water and the pH will be that of pure water, *i.e.* 7. The neutralisation of *any* strong acid is therefore given by the equation



One result of this is that the enthalpy change for this reaction, which is known as the *enthalpy of neutralisation*, is the same for all strong acids and strong bases.

In acid-base titrations, the end-point (*i.e.* the point where the amount of base added is exactly equivalent to the amount of acid taken) is usually detected by the use of an indicator. To ensure that an indicator with a suitable pH range is chosen, it is necessary to know how the pH of the solution will alter during the titration, particularly in the region of the end-point. For titrations of strong acids with strong bases the pH at any point can be calculated from the concentration of strong acid left un-neutralised ($= [\text{H}^+]$), and after the end-point the concentration of base in excess ($= [\text{OH}^-]$). The complete curve for such a titration is shown in Fig. 91, curve (a). Table 10 shows, in more detail, how the pH alters near the end-point for the addition of successive volumes of 0.05 cm^3 (about one drop) of the solution of the base. It will be seen that within one drop on either side of the end-point the pH varies from 4

TABLE 10. pH CHANGES DURING AN ACID-BASE TITRATION
(25 cm^3 of 0.1 mol dm^{-3} strong acid solution titrated with 0.1 mol dm^{-3} NaOH)

Titre (cm^3)	Excess of acid (cm^3 of 0.1 mol dm^{-3})	Excess of alkali (cm^3 of 0.1 mol dm^{-3})	$[\text{H}^+]$	$[\text{OH}^-]$	pH
24.80	0.20		0.00040		3.4
24.85	0.15		0.00030		3.5
24.90	0.10		0.00020		3.7
24.95	0.05		0.00010		4.0
25.00	neutral (end-point)				7.0
25.05		0.05		0.00010	10.0
25.10		0.10		0.00020	10.3
25.15		0.15		0.00030	10.5
25.20		0.20		0.00040	10.6

to 10. Within the normal accuracy of a titration, therefore, any indicator whose range lies within these limits can be used to determine the end-point, and the change in pH is so great at this point that the last drop of reagent will cause the indicator to change directly from its acid colour to its alkaline colour. All the indicators shown in Table 9 can be used for titrating a strong acid with a strong base.

If either the acid or base that is being titrated is weak, then owing to hydrolysis the salt solution produced at the end-point is not neutral. Fig. 91 also shows pH curves for the titration of a weak acid (ethanoic acid) with a strong base and the titration of a strong acid with a weak base (ammonia).

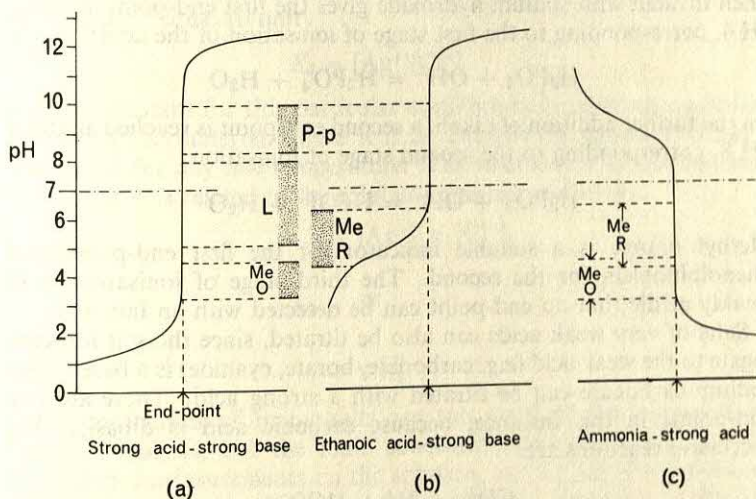


Fig. 91. pH curve for acid-base titrations, showing the indicator ranges for phenolphthalein (P-p), litmus (L), methyl red (MeR) and methyl orange (MeO)

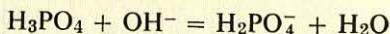
The titration curve (b) for ethanoic acid with sodium hydroxide has been obtained in the following way. Up to the end-point both a weak acid and its salt are present, so that the equation for the pH of a buffer solution (§ 14.10) can be used. After the end-point there is an excess of OH^- ions, and the pH can be found from this in the usual way. The vertical portion near the end-point occurs over the region pH 7.5–10, and the choice of a suitable indicator is considerably restricted. Methyl red, for example, would give a slow change in colour that would be complete before the end-point was reached. Phenolphthalein, however, covers part of the vertical portion of the curve and would therefore indicate the true end-point.

When a weak base (e.g. ammonia) is titrated with a strong acid, the salt solution that is formed is acid due to hydrolysis, so that the end-

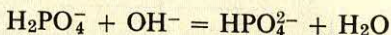
point is at a pH below 7. Curve (c) shows that the vertical portion of the curve extends from about pH 4-6.5. Both methyl orange and methyl red cover this region, and either of these indicators can be used to detect the end-point.

If both acid and base are weak, there is no vertical portion to the curve, merely a point of inflexion. No indicator is satisfactory for such a titration.

It is possible to titrate mixtures of acids, if there is a considerable difference in the strengths of the different acids. The stronger acid will be neutralised first, and the weaker one will give a separate end-point at a higher pH value. The acids may be different stages in the ionisation of a polybasic acid; for example, phosphoric acid (which is tribasic) when titrated with sodium hydroxide gives the first end-point at about pH 4, corresponding to the first stage of ionisation of the acid:

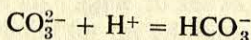


On the further addition of alkali, a second end-point is reached at about pH 8, corresponding to the second stage of ionisation:

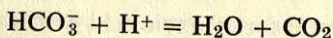


Methyl orange is a suitable indicator for the first end-point, and phenolphthalein for the second. The third stage of ionisation is so weakly acidic that no end-point can be detected with an indicator.

Salts of very weak acids can also be titrated, since the salt ion conjugate to the weak acid (e.g. carbonate, borate, cyanide) is a base. Thus sodium carbonate can be titrated with a strong acid. There are two end-points in this instance, because carbonic acid is dibasic. The successive reactions are:



which gives an end-point at about pH 8 (detected by phenolphthalein) and



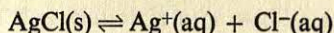
with an end-point at about pH 5, for which methyl orange is suitable. If the solution is boiled, the CO_2 is expelled and the final solution is then neutral (pH 7), so that phenolphthalein then gives the final end-point only.

14.13. Sparingly soluble electrolytes

Many ionic salts are very sparingly soluble in water, e.g. AgCl , BaSO_4 , CaCO_3 , $\text{Fe}(\text{OH})_3$, PbS . For many purposes such substances are regarded as insoluble; for example, when silver is estimated gravimetrically by precipitating and weighing as the chloride it is assumed that all the silver has been removed from solution. Within the limits

of accuracy of the determination this is true, but nevertheless a very small concentration of silver chloride remains in solution.

If a saturated solution of silver chloride is prepared by shaking the solid with water, the solution contains only silver and chloride ions in equilibrium with the solid:



and the equilibrium constant will be

$$K = \frac{[\text{Ag}^+][\text{Cl}^-]}{[\text{AgCl}]}$$

Taking the concentration of the solid, by the usual convention, as constant and equal to unity

$$K_s = [\text{Ag}^+][\text{Cl}^-]$$

and the constant for this particular equilibrium is called the *solubility product* of the material. Since it is an equilibrium constant, it has a fixed value for any one temperature. The solubility S of the material, in mol dm^{-3} , is related to the solubility product as follows:

$$S = [\text{Ag}^+] = [\text{Cl}^-]$$

so that

$$K_s = S^2$$

and

$$S = \sqrt{K_s}$$

The solubilities of many salts are too small to be measured by chemical analysis, but the ionic concentrations can be found from conductance measurements on the solution, and the solubility product thus obtained. Some values of solubility products are given in Table 11.

TABLE 11. SOLUBILITY PRODUCTS (K_s AT 25°C)

Sulphides		Hydroxides	
Bi_2S_3	10^{-97}	Fe(OH)_3	10^{-37}
Sb_2S_3	1.7×10^{-93}	Al(OH)_3	2.0×10^{-32}
HgS	1.5×10^{-52}	Cr(OH)_3	6×10^{-31}
CuS	6×10^{-36}	Zn(OH)_2	7.1×10^{-18}
CdS	8×10^{-27}	Ni(OH)_2	3×10^{-16}
SnS	1.0×10^{-25}	Co(OH)_2	6×10^{-16}
ZnS	2.5×10^{-22}	Fe(OH)_2	8×10^{-16}
CoS	4×10^{-21}	Mn(OH)_2	1.9×10^{-13}
NiS	3×10^{-19}	Mg(OH)_2	1.8×10^{-11}
MnS	2.5×10^{-10}		

The presence of a common ion—*e.g.* in the case of silver chloride either the Ag^+ or the Cl^- ion—will affect the solubility: if silver chloride is shaken with a solution of sodium chloride, the high concentration of

chloride ions reduces the silver ion concentration compared with what it would be in pure water, since the product $[Ag^+][Cl^-]$ must remain constant. This is known as the *common ion effect*, and the result is that *the solubility of a sparingly soluble salt is reduced by the presence of a common ion.*

EXAMPLE

The solubility product of silver chloride is 2.8×10^{-10} at $25^\circ C$. What is the solubility (a) in pure water, and (b) in 0.1 mol dm^{-3} NaCl solution, at this temperature?

$$\begin{aligned} (a) \quad S &= \sqrt{K_s} \\ &= \sqrt{2.8 \times 10^{-10}} \\ &= 1.7 \times 10^{-5} \text{ mol dm}^{-3} \end{aligned}$$

$$\begin{aligned} (b) \quad K_s &= [Ag^+][Cl^-] \\ &= S \times 0.1 \\ S &= \frac{2.8 \times 10^{-10}}{0.1} \\ &= 2.8 \times 10^{-9} \text{ mol dm}^{-3} \end{aligned}$$

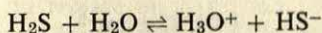
The solubility product is of considerable importance in analysis because it fixes the conditions under which a metal can be precipitated as a sparingly soluble salt. Solid silver chloride is in equilibrium with a solution containing Ag^+ and Cl^- when the product of the ionic concentrations is equal to K_s , i.e. $[Ag^+][Cl^-] = 2.8 \times 10^{-10}$. If the product $[Ag^+][Cl^-]$ falls below this figure, silver chloride will dissolve; conversely, when the concentrations of the ions give a product greater than K_s , silver chloride will be precipitated.

When a solution contains several metal ions, advantage can be taken of differences in the solubility products of their salts to achieve some separation. Many metals, for example, form sparingly soluble sulphides (see figures for K_s in Table 11), and these can be divided into two groups: those with solubility products of 10^{-25} or less (Bi, Sb, Hg, Cu, Cd, Sn) and those greater than 10^{-22} (Co, Ni, Zn, Mn). Precipitation of any of these metals will occur when the solution contains a sufficient concentration of sulphide ions for the solubility product for that metal to be exceeded, i.e.:

$$[\text{Metal ion}][S^{2-}] > K_s$$

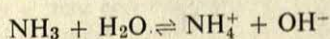
In qualitative analysis, the concentration of any metal ion in the prepared solution is roughly constant (within, say, a factor of ten), so that if the sulphide ion concentration is adjusted to make the product $[\text{Metal ion}][S^{2-}]$ about 10^{-24} , all the first group of metals will be precipitated, but none of the second group. It is quite easy to produce the very low concentration of sulphide ions required (about $10^{-23} \text{ mol dm}^{-3}$),

by acidifying the solution with HCl and then dissolving hydrogen sulphide in it. H_2S , being dibasic, dissociates as follows:



The second stage of dissociation is very weakly acidic, and the degree of dissociation is reduced even further by the high concentration of hydrogen ions due to the hydrochloric acid, so that $[\text{S}^{2-}]$ has the required value. It is important that the concentration of hydrochloric acid should be correct. If it is too strong, the sulphide ion concentration will be too small to precipitate some of the metals that should be removed (*e.g.* Cd), while if it is too weak some metals of the other group may also precipitate.

The precipitation of Fe, Cr and Al as hydroxides is arranged in the same way. In this case it is the concentration of OH^- ions that must be controlled, so that the product $[\text{Metal ion}][\text{OH}^-]$ is greater than the solubility products of the hydroxides of these metals, but less than those of Zn, Ni, Co, Mn and Mg. This is done by making the solution alkaline with ammonia, in the presence of ammonium chloride. The excess of ammonium ions provided by the ammonium chloride decreases the ionisation of the ammonia, for which the equilibrium is:



In this way the concentration of hydroxyl ions can be kept within the correct limits. The solubility product of iron(II) hydroxide is similar to that of cobalt and nickel, but precipitation of iron can be achieved by oxidising it to the iron(III) state before the ammonia is added.

Zn, Ni, Co and Mn are precipitated as sulphides from an alkaline solution saturated with H_2S . The effect of the low hydrogen ion concentration is to increase the degree of ionisation of the H_2S , so that the sulphide ion concentration is large enough for the solubility product of the sulphides of these metals to be exceeded.

The separation of metals by controlled precipitation is actually more complicated than the above explanation suggests. Another important factor is the formation of complex ions (*see* § 14.14). In the precipitation of metals as hydroxides, for example, the solubility of many metals is increased by the presence of ammonia, with which they react to form complexes.

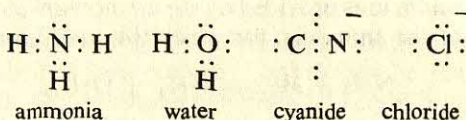
In gravimetric analysis, metals are often precipitated in the form of a sparingly soluble salt; for example, barium can be estimated from the mass of barium sulphate obtained. It is important to make sure that the amount left in solution is negligible (within the limits of accuracy required), and it may be necessary to reduce the solubility by making use of the common ion effect. The solubility product of BaSO_4 is 1.08×10^{-10} at 25°C , so that the solubility would be:

$$\begin{aligned}
 S &= \sqrt{1.08 \times 10^{-10}} \\
 &= 1.04 \times 10^{-5} \text{ mol dm}^{-3} \\
 &= 0.00242 \text{ g dm}^{-3}
 \end{aligned}$$

This would represent an appreciable error, but the solubility can be reduced to a negligible amount by adding a small excess of sulphate ions after the precipitation is complete. A further loss may occur during the washing of precipitates, and this can again be reduced by washing with a solution containing a common ion instead of with water. In the case of barium sulphate a dilute solution of ammonium sulphate can be used.

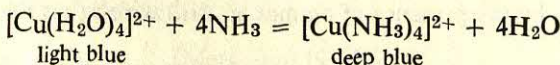
14.14. Complex ions

Metal ions in solution often exist as complex structures, in which other molecules or ions are chemically bound to the metal by dative (co-ordinate) bonds. Most metals of the transition block can form complex ions in this way, as explained in § 3.3. Groups that form dative bonds by contributing a lone pair of electrons are called *ligands*, the following being some of the more important examples:



Water is the most common ligand, and many metal ions are hydrated (even in the solid state) by water molecules that are chemically bound to the ion; this is in addition to any water molecules that may attach themselves to the ion in solution by electrical attraction. Hydration is often the cause of colour in ions; for example, anhydrous copper(II) sulphate (containing the ion Cu^{2+}) is colourless, but a solution of copper(II) sulphate is blue due to the hydrated ion $[\text{Cu}(\text{H}_2\text{O})_4]^{2+}$. Other examples of complex hydrates are $[\text{Al}(\text{H}_2\text{O})_6]^{3+}$, $[\text{Cr}(\text{H}_2\text{O})_6]^{3+}$, $[\text{Fe}(\text{H}_2\text{O})_6]^{2+}$ and $[\text{Ni}(\text{H}_2\text{O})_4]^{2+}$.

If a more reactive ligand is added, some or all of the water molecules may be replaced. On the addition of ammonia to a solution of copper(II) sulphate, the tetraamminecopper(II) ion is formed:



The change is easily detected by the deepening of the colour. When the ammonia is first added a precipitate of copper(II) hydroxide is formed, but redissolves on the addition of more ammonia. This illustrates another possible effect of the formation of complex ions: an increase in solubility. The precipitated copper(II) hydroxide has a very low solubility product (about 10^{-19}), so that the concentration of Cu^{2+} ions in a

saturated solution is extremely small. In the presence of ammonia, however, the Cu^{2+} ions react to form the complex, and more copper(II) hydroxide dissolves to replace the Cu^{2+} ions removed in this way. If sufficient ammonia is added, the whole of the precipitate will dissolve. Similarly, the addition of potassium cyanide to a solution of a silver salt first causes a precipitate of silver cyanide, but the latter dissolves in an excess of cyanide due to the formation of a complex silver ion:



In this case the charge on the complex ion differs from that of the original metal ion, because the ligand is also charged. Sparingly soluble silver salts also dissolve in ammonia with the formation of the complex ion $[\text{Ag}(\text{NH}_3)_2]^+$.

QUESTIONS

G.C.E.

1. Define the terms *electrolytic conductivity*, κ , *molar conductivity*, Λ , and *cell constant*, C , and give the equations which relate them. How are the values of molar conductivity at zero concentration, Λ_0 , obtained accurately from experimental values of the molar conductivity for strong electrolytes at finite concentrations?

Calculate the degree of dissociation and the concentration of hydrogen ions in aqueous ethanoic (acetic) acid of concentration 0.10 mol dm^{-3} . (K_a for ethanoic acid = 1.75×10^{-5} .)

The *resistance* of a conductance cell containing the same solution of ethanoic acid is 100Ω . Will the *resistance* be higher or lower when the conductance cell contains the following aqueous solutions: (a) ethanoic acid of concentration $0.010 \text{ mol dm}^{-3}$, (b) potassium chloride of concentration 0.10 mol dm^{-3} , (c) hydrochloric acid of concentration $0.0010 \text{ mol dm}^{-3}$? Give reasons for your answers. [O. & C.]

2. (a) What do you understand by the term *molar conductivity* as applied to an electrolyte? (b) Show graphically how the molar conductivity changes with increasing dilution for (i) a strong electrolyte, (ii) a weak electrolyte. Give one example of each type of electrolyte. Account briefly for the changes you have suggested.

(c) The molar conductivity of aqueous ethanoic (acetic) acid of concentration 0.1 mol dm^{-3} , was $4.6 \text{ S cm}^2 \text{ mol}^{-1}$ ($\Omega^{-1} \text{ cm}^2 \text{ mol}^{-1}$), and at infinite dilution $352 \text{ S cm}^2 \text{ mol}^{-1}$ ($\Omega^{-1} \text{ cm}^2 \text{ mol}^{-1}$). Calculate (i) the degree of dissociation of the acid at this concentration, (ii) the pH of the solution.

(d) What substance would you add to a solution of ethanoic acid in order to make a solution the pH of which is almost unaffected by the addition of small quantities of acid or alkali? What is the name given to such a mixture? Explain briefly how it works. [A.E.B., 1978]

3. (a) Define pH. (b) If the pH of a 0.1 mol dm^{-3} solution of ethanoic (acetic) acid is 2.88 at 20°C , calculate (i) the hydrogen ion concentration of the

solution at 20°C, (ii) the dissociation constant K_a for ethanoic (acetic) acid at 20°C.

(c) A 1 mol dm⁻³ solution of hydrofluoric acid has a pH of 1.7 whilst a 1 mol dm⁻³ solution of hydrochloric acid has a pH of 0. State which is the stronger acid, and give an explanation in terms of the hydrogen-halogen bonds. [J.M.B.]

4. (a) Ammonia in aqueous solution is a weak base, its dissociation constant, K_b , being about 1×10^{-5} mol dm⁻³. (i) What is the pH of a 0.1 mol dm⁻³ aqueous solution of ammonia? [Ionic product of water (at 25°C), $K_w = 1 \times 10^{-14}$ mol² dm⁻⁶.] (ii) Describe qualitatively how the answer in (i) would be affected by the addition of solid ammonium chloride.

(b) The solubility products of magnesium hydroxide and calcium hydroxide at a certain temperature are given below:

	solubility product/mol ³ dm ⁻⁹
Mg(OH) ₂	1×10^{-11}
Ca(OH) ₂	1×10^{-6}

Separate solutions of concentration 0.2 mol dm⁻³ with respect to Mg²⁺(aq) and Ca²⁺(aq) ions are independently mixed with equal volumes of 0.2 mol dm⁻³ NH₃(aq). In each case, deduce whether or not a precipitate of the metal hydroxide forms. [Cambridge]

5. (a) Define pH. (b) What is meant by the ionic product of water and what is its accepted value at 298 K? (c) The degree of ionization of water increases with temperature. State whether you would expect the pH of pure water at 353 K to be numerically greater than, less than or equal to 7. Give your reasons. (d) What is the pH of each of the following aqueous solutions? (You may assume 100% dissociation.) (i) 10⁻³ mol dm⁻³ potassium hydroxide; (ii) 2 × 10⁻³ mol dm⁻³ hydrochloric acid.

(e) The following table lists the pH values of 1 mol dm⁻³ solutions of different solutes. Which of the solutes do you think are *strong acids*, *weak acids*, *strong bases* and *weak bases*?

Solute	P	Q	R	S	T	U
pH	7.8	0.1	5.2	14.0	0.0	12.1

(f) A solution containing 0.1 mol dm⁻³ of acetic acid and 0.4 mol dm⁻³ of sodium acetate has a pH of 5.35. (i) Write down the expression for the dissociation constant of acetic acid in aqueous solution. (ii) Use the above information to calculate a value for the dissociation constant. [London]

6. (a) Draw diagrams to show the approximate change in pH when (i) aqueous sodium hydroxide solution of concentration 0.1 mol dm⁻³ is added, in portions, to 25 cm³ of an aqueous solution of ethanoic acid (acetic acid) of concentration 0.1 mol dm⁻³, (ii) aqueous ammonia solution of concentration 0.1 mol dm⁻³ is added, in portions, to 25 cm³ of an aqueous solution of hydrochloric acid of concentration 0.1 mol dm⁻³. (b) By reference to these diagrams, explain the principle which underlies the choice of indicators in acid/alkali titrations. Give the name of an indicator suitable for each of the titrations in (a) and give its colours in acid and alkaline solutions.

(c) Write equations for the reactions which take place when (i) ethanoic acid, (ii) aminoethane are separately dissolved in water. Explain why the

first is an acid, and the second is a base. (d) Write an equation for the reaction which takes place when aminoethanoic acid, $\text{H}_2\text{N}-\text{CH}_2-\text{COOH}$, dissolves in water, and suggest why the solution is nearly neutral. [A.E.B., 1977]

7. Explain what is meant by *solubility product*. The solubility of anhydrous calcium iodate(V) in water at 298 K is 3.07 g dm^{-3} . Calculate (a) its solubility product, (b) its solubility (in g dm^{-3}) in an aqueous solution containing 0.1 mol dm^{-3} of sodium iodate(V).

Explain, with full experimental details, how you would determine the solubility of calcium iodate(V) in water at 298 K, emphasising any precautions you would have to take. [$A_r(\text{Ca}) = 40$; $A_r(\text{I}) = 127$; $A_r(\text{O}) = 16$.] [W.J.E.C.]

CHAPTER 15

CHEMICAL CELLS AND ELECTROLYSIS

15.1. Electrode reactions

We have seen that a metal, in the solid state, consists of metal ions together with the valence electrons that bind them together (§ 3.6). If a metal is in contact with a solution of one of its salts, the ions in the metal will tend to come into equilibrium with those in solution. This process differs from the equilibrium established between a compound and its saturated solution, because when an ion leaves the metal the associated valence electrons are left behind, thus giving the metal a negative charge. Conversely, if an ion from solution enters the crystal lattice of the metal, the latter gains a positive charge.

The establishment of equilibrium depends on the following opposing processes:

(a) *Metal passing into solution as metal ions*

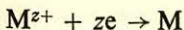


where the whole number z represents the *charge number* of the ion, so that z electrons are left behind in the metal. It must be remembered that the ions will actually be hydrated in solution, so that the amount of energy required to liberate the metal ions from the crystal lattice will be partly offset by the energy evolved by the hydration. The rate of process (a) will depend upon the following factors:

- (i) The nature of the metal and the extent of hydration of its ions.
- (ii) The temperature.
- (iii) The potential difference between the metal and the solution.

If such a potential difference exists, it will tend either to hinder or to assist the passage of ions into solution, depending on whether the solution or the metal is the more positive.

(b) *Ions discharging at the metal electrode*



The rate of this process will depend on the same three factors given above, and in addition:

- (iv) The concentration of the ions in solution. This factor does not arise in (a) because the "concentration" of a solid is constant.

When the metal is first placed in the solution, the rate of either (a) or (b) will be the greater, depending on the conditions. Metals have low electronegativities (*see* Table 1) and therefore have a strong tendency

to pass into solution as positive ions; let us assume, therefore, that the conditions are such that process (a) is the faster. This means that more metal ions pass into solution than are discharged, so that the solution gains positive ions and the metal acquires a negative charge. The charged metal exerts a strong electrical attraction on positive ions in solution, so that many of these are held close to the surface, the result being what is called an *electrical double layer* (Fig. 92). Since the two sides of the double layer, in the metal and the solution respectively, have charges of opposite sign, there is now a potential difference between metal and solution. A positive ion leaving the metal is hindered by the presence of this potential difference, and the rate of process (a) is slowed down, while at the same time positive ions can more easily pass across the double layer towards the metal and therefore process (b) is speeded up. When the two rates become equal, equilibrium has been established in the reversible reaction

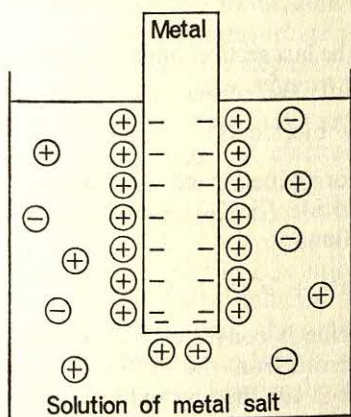
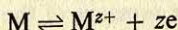


Fig. 92. Electrical double layer

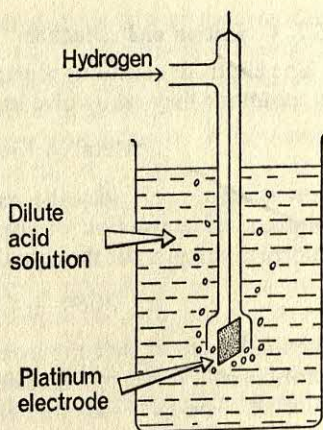
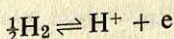


Fig. 93. Hydrogen electrode

and the potential difference between metal and solution will remain at a constant value. Equilibrium is established quickly, because the reaction is restricted to a very small region around the electrode. Outside this, there is no change, so that the concentration of the salt solution is not affected.

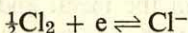
Potential differences at electrodes are not restricted to metals. Hydrogen can also pass into solution as hydrogen ions (H_3O^+), owing to its affinity for water when in the ionic form. The reversible reaction



can take place, but as the hydrogen is in the gaseous state a metal

electrode must be in contact with the hydrogen to act as a charge carrier. A simple type of hydrogen electrode is shown in Fig. 93. The gas is bubbled out of the end of a tube, in which there is an electrode of platinum.

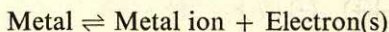
Elements with a high electronegativity (*e.g.* the halogens) have a tendency to form negative ions. Chlorine, for example, can take part in the reversible reaction



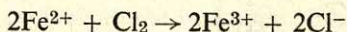
and a potential difference will again be set up between a platinum electrode in contact with the gas, and a solution containing chloride ions. An electrode similar to the hydrogen electrode in Fig. 93 can be used. With any gas electrode, the rate at which the substance passes into solution as ions will depend on the concentration of molecules in the gas, in addition to the other factors listed above, so that the potential difference will vary with the pressure of the gas.

15.2. Oxidation and reduction

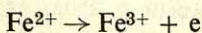
The electrode reactions illustrated in the last section have one feature in common: they all involve an *electron transfer*, *e.g.*



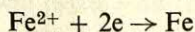
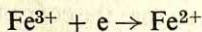
Now compare this with the oxidation or reduction of a metal ion in solution. If a solution of iron(II) chloride (FeCl_2) is oxidised with chlorine, we can write the equation as follows:



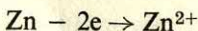
The final result is that the iron(II) chloride is converted into iron(III) chloride, as a result of a transfer of electrons from the Fe^{2+} ions to the chlorine. The Fe^{2+} ions lose electrons and are thereby oxidised to the iron(III) state:



Conversely, a solution of iron(III) chloride can be reduced (*e.g.* with zinc and hydrochloric acid), first to the iron(II) state and then to metallic iron,



while the reducing agent loses the electrons that are gained by the iron, *e.g.*



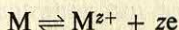
as the zinc dissolves in the form of zinc ions.

Oxidation and reduction in solution can therefore be defined quite simply in the following terms:

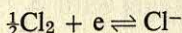
Oxidation is a process that results in the loss of electrons.

Reduction is a process that results in the gain of electrons.

It follows that an electrode reaction always involves both the oxidised and the reduced state of a substance. For a metal electrode:



the electrode itself is the reduced state, and the metal ions in solution the oxidised state. In the case of a non-metal, or anion, electrode, e.g.

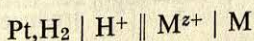


the chlorine gas is the oxidised state, and the chloride ions the reduced state.

15.3. Electrode potentials

It is not possible to measure the potential difference of a single electrode because the measuring instrument would have to be in electrical contact with both the electrode and the solution, and this would involve placing a second electrode in the solution. It is, in fact, only possible to measure the *difference* in potential between two electrodes. If, however, one particular type of electrode is adopted as a *standard reference electrode*, then the potentials of all other electrodes can be compared with it. The electrode chosen for this purpose is the *standard hydrogen electrode*, which is a hydrogen electrode with the gas at a pressure of 101 kPa, immersed in a solution containing hydrogen ions equivalent to a 1 mol dm⁻³ ideal solution. If, for example, the potential of a metal electrode is required, then the latter is combined with a standard hydrogen electrode to form a complete cell: this could be arranged as shown in Fig. 94. Electrical connection between the two electrolytes is made, in this case, by means of a *salt bridge* consisting of a jelly containing a high concentration of potassium chloride. The electromotive force of the cell could be measured with a potentiometer, as shown. This method is suitable because when the balance point is reached there is no current flowing through the cell. Any current flow will cause the electrode reactions to proceed in one particular direction, thus upsetting the equilibrium.

The cell shown in Fig. 94 can be represented diagrammatically as:



and the *electrode potential* of the metal M is defined as the e.m.f. of the cell. This is equivalent to assuming that the electrode potential of hydrogen is zero. The potential of the standard hydrogen electrode is constant, because the pressure of the gas and the concentration of the

hydrogen ions in solution are fixed: however, the potential of the metal electrode will vary with the ionic concentration. In order to compare the electrode potentials of different elements, a standard 1 mol dm^{-3} ionic concentration is chosen (assuming ideal behaviour), so that the *standard electrode potential* of a metal is the e.m.f. of the cell

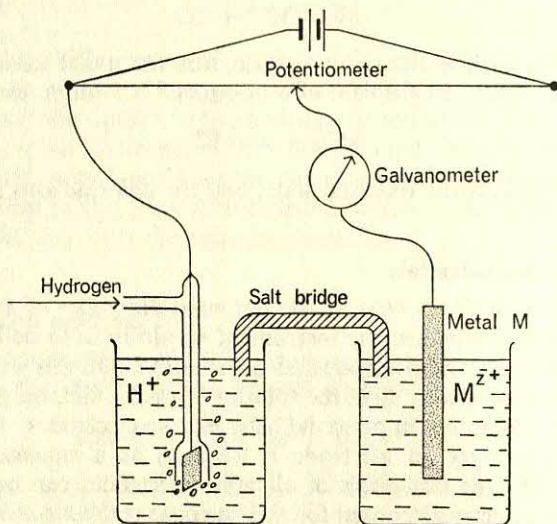
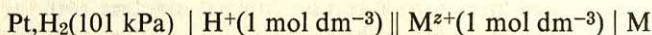


Fig. 94. Measurement of electrode potential

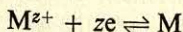
The variation of the e.m.f. of an electrode with concentration is given by the Nernst equation:

$$E = E^\ominus + \frac{RT}{zF} \ln \frac{[\text{oxidised state}]}{[\text{reduced state}]}$$

where $E^\ominus$ is the standard electrode potential and T the temperature in kelvin. R is the gas constant, F is a quantity of electricity known as the Faraday constant (*see* p. 264) and z is the number of electrons transferred in the electrode reaction. Putting in the values of the constants and taking the temperature as 298 K, the equation becomes:

$$E = E^\ominus + \frac{0.059}{z} \log_{10} \frac{[\text{oxidised state}]}{[\text{reduced state}]}$$

Thus for an electrode of a metal M , giving M^{z+} ions, the oxidised state is M^{z+} and the reduced state is the metal itself, while the number of electrons transferred is equal to z :



so that the e.m.f. of the electrode is given by

$$E = E^\ominus + \frac{0.059}{z} \log_{10} [M^{z+}]$$

the concentration of the metal being put equal to unity, since it is a pure solid.

For an anion electrode, e.g. $\frac{1}{2}\text{Cl}_2 + e \rightleftharpoons \text{Cl}^-$, the chlorine gas is the oxidised state and its concentration can be expressed in terms of the pressure. With chlorine gas at 101 kPa pressure, the e.m.f. would vary with the concentration of the chloride ions in the following way:

$$E = E^\ominus + 0.059 \log_{10} \frac{1}{[\text{Cl}^-]}$$

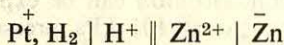
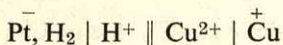
z in this case being equal to 1.

The standard electrode potential has a characteristic value for a particular element at any one temperature. Table 12 gives a list of standard electrode potentials arranged in order of increasing value; such a list is often called the "electrochemical series". The sign given to an electrode potential has to be decided by adopting some convention, and is fixed in the following way: the cell diagram is written with the standard hydrogen electrode on the left-hand side, and if a measurement

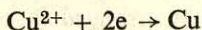
TABLE 12. STANDARD ELECTRODE POTENTIALS AT 25°C

<i>Electrode</i>	<i>E</i> [⊖] (V)
Li ⁺ /Li	−3.03
K ⁺ /K	−2.92
Ca ²⁺ /Ca	−2.87
Na ⁺ /Na	−2.71
Mg ²⁺ /Mg	−2.37
Al ³⁺ /Al	−1.66
Zn ²⁺ /Zn	−0.76
Fe ²⁺ /Fe	−0.44
Cd ²⁺ /Cd	−0.40
Ni ²⁺ /Ni	−0.25
Sn ²⁺ /Sn	−0.14
Pb ²⁺ /Pb	−0.13
H ⁺ /H ₂ , Pt	0.00
Cu ²⁺ /Cu	+0.34
O ₂ /OH [−] , Pt	+0.40
I ₂ /I [−]	+0.54
Hg ₂ ²⁺ /Hg	+0.80
Ag ⁺ /Ag	+0.80
Br ₂ /Br [−]	+1.07
Cl ₂ /Cl [−]	+1.36
Au ³⁺ /Au	+1.50

of the e.m.f. of the cell shows the *right-hand* electrode to be the positive pole, the sign of the electrode potential is taken to be *positive*.* For example, copper has a positive potential (with respect to hydrogen) and zinc a negative potential, so that the cells formed by combining these electrodes with a hydrogen electrode would show the following polarities:



It is also useful to examine the direction in which current will flow inside such a cell if the electrodes are connected externally by a wire; Fig. 95 illustrates what will happen in the case of the hydrogen-copper cell. It will be seen that positive current travels from left to right across the cell, so that the reaction occurring at the copper electrode is the discharge of copper ions



i.e. a reduction reaction. The more positive the electrode potential of the metal, therefore, the greater is the tendency for the metal ions to be reduced to the metal. For this reason, the electrode potential can be referred to as a *reduction potential*.

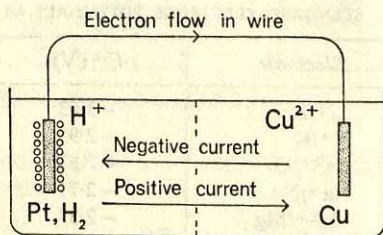
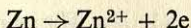


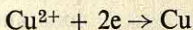
Fig. 95. Current flow in a hydrogen-copper cell. Positive current is carried by the H^+ and Cu^{2+} ions, negative current by the anions (*e.g.* Cl^- if the electrolytes are hydrochloric acid and copper(II) chloride)

It follows that the electrochemical series can be used to find the relative ease of *reduction* of an element (shown by how *positive* is the electrode potential), or the relative ease of *oxidation* (shown by an increasing *negative* value). Thus a rod of zinc dipped into a solution of copper sulphate will start to dissolve and copper metal will be deposited onto it, because zinc has a more negative potential than copper and will be oxidised:

* This sign convention is the one recommended by the International Union of Pure and Applied Chemistry. In America, however, a different convention is used, so that in American textbooks e.m.f. values are of the opposite sign to those given here.



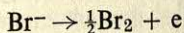
while the copper is at the same time reduced:



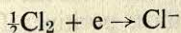
so that the complete reaction gives the equation:



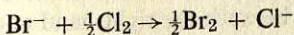
This is sometimes described as zinc displacing copper from solution. In the same way, bromine is more negative than chlorine, so that bromide ions can be oxidised by chlorine:



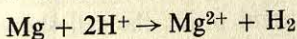
while the chlorine is itself reduced:



The net result is that the bromine is displaced by the chlorine:



Metals which are more negative than hydrogen can displace hydrogen ions from acid solutions, *i.e.* the metal is oxidised to metal ions and passes into solution, while the hydrogen ions are reduced to hydrogen, which is evolved as a gas, *e.g.*:



Many metals above hydrogen do not dissolve in cold dilute acid, but this is due to the fact that the speed of the above reaction is very slow, owing to secondary effects, of which the presence of oxide films on the surface of the metal is one (*see* § 15.8). The position of a metal in the electrochemical series shows the relative tendency towards oxidation but does not give any information about the rate at which it will occur.

The ease of oxidation of an element by gaseous oxygen is also approximately shown by the value of its electrode potential. Thus gold (1.50 V) is not oxidised in air, while sodium (−2.71 V) reacts vigorously. Again, many metals react very slowly with oxygen at ordinary temperatures (*e.g.* nickel, chromium, aluminium) and so appear not to be affected.

15.4. Chemical cells

Combination of two different electrode systems (sometimes called *half-cells*) produces a chemical cell. The use of the hydrogen electrode to measure electrode potentials has already provided examples of one type of cell. Another type, where the electrodes consist of two different metals in contact with a solution of their ions, is illustrated by the Daniell cell (Fig. 96). Here the electrodes are of zinc and copper, in contact with zinc sulphate and copper sulphate solutions respectively.

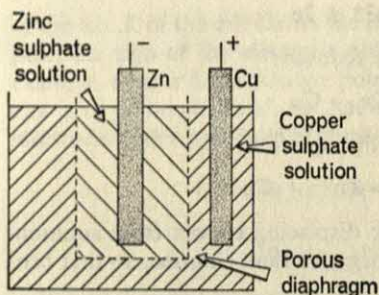
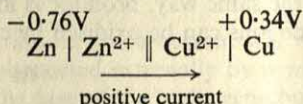


Fig. 96. The Daniell cell

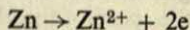
The two electrolytes are separated by a diaphragm (such as a porous pot) which allows the passage of ions, and therefore electric current, through the cell when the two electrodes are connected by means of an external circuit.

The Daniell cell can be written diagrammatically:

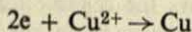


The cell is written, in accordance with the sign convention, so that the right-hand electrode is the more positive; if the cell is allowed to pass current through an external circuit, positive current will flow inside the cell from left to right, as shown. The e.m.f. of the cell will be the difference in potential between the right-hand and left-hand electrodes, *i.e.* $0.34 - (-0.76) = 1.10 \text{ V}$. As these are the standard electrode potentials for copper and zinc this gives the standard e.m.f. of the cell at 25°C , *i.e.* for ionic concentrations of 1 mol dm^{-3} . The e.m.f. will vary somewhat with changes in both temperature and the concentrations of the electrolytes.

The direction of current inside the cell shows that, when the cell supplies current, zinc passes into solution at the left-hand electrode:



while at the right-hand electrode, copper ions are discharged:



so that the reaction taking place in the cell as a whole is the reduction of copper ions by zinc:



This equation is obtained by adding together the individual electrode reactions, remembering that the same amount of current must pass through both electrodes, so that the equations must be balanced to ensure that the same number of electrons is transferred in each reaction.

When the cell is on open circuit, the electrode reactions are in equilibrium and no chemical change occurs. When the cell is supplying current, the cell reaction takes place and will continue to do so until either the concentration of the copper solution has fallen to a very low value or else the zinc electrode has entirely dissolved.

The electrical energy produced by a cell is directly due to the chemical

reaction taking place inside the cell, *i.e.* chemical energy is being converted into electrical energy.

15.5. Electrolysis

Imagine a cell formed by dipping two platinum electrodes into a solution of copper(II) chloride. Since the two electrodes are identical the e.m.f. of the cell will be zero. In order to pass a current through the cell an external e.m.f. must be applied, as shown in Fig. 97. This shows an arrangement whereby the applied e.m.f. can be altered at will by moving the sliding contact on the potentiometer, while the current and applied voltage can be measured on the ammeter and voltmeter. The direction of positive current in the cell is from right to left, so that positive ions (Cu^{2+}) will discharge at the left-hand electrode (which is

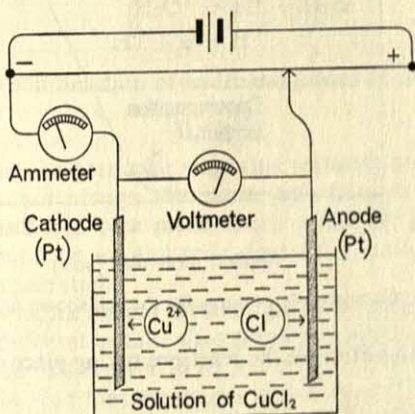


Fig. 97. Electrolysis of a solution of copper(II) chloride between platinum electrodes

therefore the cathode), while the negative Cl^- ions will discharge at the right-hand electrode (which is the anode). The cathode tends to become covered with a layer of metallic copper, while chlorine gas tends to be liberated at the anode. Liberation of materials at the electrodes in this way is known as *electrolysis*. It will be seen in a later example that in some cases, instead of material being liberated at an electrode, the electrode itself may dissolve.

The result of electrolysis in the above example will be to convert the cathode into a copper electrode, and the anode into a chlorine electrode. The electrode potentials of copper and chlorine are 0.34 V and 1.36 V respectively, so that the cell will acquire an e.m.f. of $1.36 - 0.34 = 1.02$ V, with the chlorine the positive pole, *i.e.* the cell e.m.f. will be in opposition to the applied e.m.f. If, at the start of the experiment, the applied e.m.f. is small, only a very small current will pass (limited by the rate at which the products of electrolysis can

diffuse away from the electrodes). As the applied voltage is increased there will be increasing concentrations of copper and chlorine at the electrodes, until a voltage is reached which can overcome the e.m.f. of the copper-chlorine cell, after which the current through the cell will increase rapidly (see Fig. 98) and copper will be continuously deposited on the cathode and chlorine gas liberated at the anode. The applied e.m.f. required to cause continuous electrolysis is known as the *decomposition potential*.

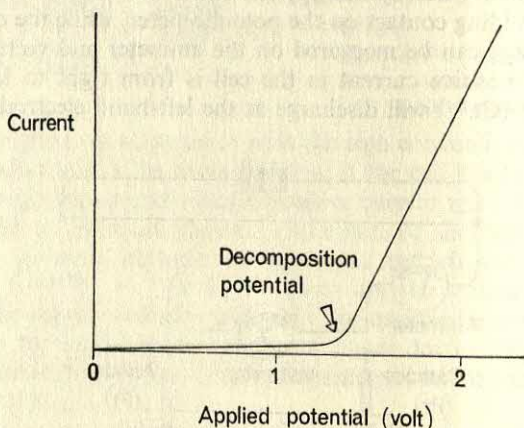
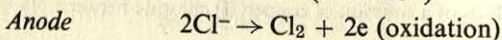
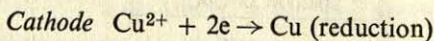
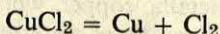


Fig. 98. Current-voltage curve for the cell shown in Fig. 97.

We see that in this example the reactions taking place at the electrodes are:



so that in electrolysis, reduction occurs at the cathode and oxidation at the anode. The overall reaction in the cell illustrated is therefore:



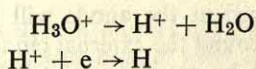
The external battery supplies the electrical energy necessary to maintain the flow of electrons from anode to cathode, at a potential difference equal to the back e.m.f. of the cell. The current, and therefore the rate at which electrolysis occurs, depends on the applied e.m.f. *in excess of the decomposition potential* (see Fig. 98, the steep portion of the graph) and obeys Ohm's law:

$$\text{Current} = \frac{\text{Excess potential}}{\text{Internal resistance of cell}}$$

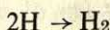
It might be expected that the decomposition potential would be equal to the normal e.m.f. of the cell set up by the products of electrolysis,

which has already been shown to be 1.02 V for the copper-chlorine cell. In fact, the decomposition potential is 1.34 V, which is higher than the theoretical value by 0.32 V. This additional potential is called the *overpotential*, and arises because the standard electrode potentials are measured under conditions of equilibrium, whereas when ions are being continuously discharged the electrode may no longer be in equilibrium with the ions in solution.

It is found that overpotentials are particularly high when gases (especially hydrogen and oxygen) are liberated. This is thought to be due to one stage in the process of discharge of the ions being relatively slow. The liberation of hydrogen at an electrode, for example, involves first the removal of a proton from the hydrogen ion and its neutralisation by an electron:



followed by the combination of hydrogen atoms to form molecules:



It is probable that the particular stage that is mainly responsible for the overpotential is not always the same, but depends on the current density. The discharge of a metal ion is a simpler process, and the deposition of metal on an electrode does not usually give rise to an appreciable overpotential.

Table 13 shows some figures for hydrogen and oxygen overpotentials at electrodes of different metals. Overpotentials increase if the current is increased, and the values given in the table all refer to the same current density. It will be seen that the figures vary with the nature of the electrode, and that the physical state of the metal is also important, as shown by the difference between smooth platinum and an electrode that has been "platinised" (*i.e.* covered with a layer of platinum black), which increases the effective surface area of the electrode. Overpotentials are of considerable practical importance in electrolysis, since they may

TABLE 13. HYDROGEN AND OXYGEN OVERPOTENTIALS
(Current density = 10 A.m⁻²)

Electrode	Overpotential (V)	
	Hydrogen	Oxygen
platinum (blackened)	0.01	0.46
platinum (smooth)	0.09	1.11
nickel	0.33	0.60
iron	0.40	0.41
silver	0.44	0.60
chromium	0.5	0.58
lead	0.67	0.80
mercury	1.04	—

be the deciding factor as to the nature of the products that will be obtained at the electrodes.

When electrolysis is taking place in a cell, electrons are liberated at the anode (e.g. by the discharge of negative ions), driven round the external circuit by the battery, and at the cathode combine with the discharging positive ions. The current is a measure of the rate at which electrons pass round the circuit; the actual *quantity* of electricity that passes in a given time can be found by multiplying the current by the time for which it is passed, the unit being the coulomb:

$$\begin{aligned}\text{Quantity of electricity} &= \text{Current} \times \text{Time} \\ \text{number of coulombs} &= \text{amps} \times \text{seconds}\end{aligned}$$

Considering the cell shown in Fig. 97, it is evident that the number of chloride ions discharged at the anode will be equal to the number of electrons that pass round the external circuit, so that the amount of chlorine liberated will be proportional to the quantity of electricity passed. This was first discovered experimentally by Faraday in 1833, and is stated in *Faraday's first law of electrolysis: the amount of any substance liberated or dissolved by the chemical action of an electric current is proportional to the quantity of electricity passed.*

Turning now to the cathode in the above cell, the discharge of each copper ion will require two electrons, since the Cu^{2+} ion has two positive charges. Since the same quantity of electricity must pass through the whole circuit in a given time, it follows that two chloride ions will discharge at the anode for each copper ion discharging at the cathode. Since one mole of *any* ion contains the same number of ions, discharge will take place in the proportion of one mole of Cl^- for every half mole of Cu^{2+} . This was discovered experimentally by Faraday and is stated in his *second law of electrolysis: the amounts (in moles) of different substances liberated or dissolved by the same quantity of electricity are inversely proportional to the charge numbers of the ions.*

The quantity of electricity that will discharge one mole of an ion is equal to the total charge on the ions. If an ion has a charge number of z (e.g. for Cl^- , $z = 1$; for Cu^{2+} ions, $z = 2$), then:

$$\text{Charge on one ion} = ze$$

$$\text{Charge on 1 mole of ions} = Lze$$

where L is the Avogadro constant.

Le is a definite, and constant, quantity of electricity known as the *Faraday constant*. The value of the Faraday can either be calculated from the electronic charge and the Avogadro constant, or it can be measured experimentally, e.g. by passing a measured quantity of electricity through a cell containing a silver anode and platinum cathode, with silver nitrate solution as electrolyte. The silver deposited on the

cathode can be accurately weighed, and it is found that 1 coulomb deposits 0.001118 g of silver. The relative atomic mass of silver is 107.9, so that one mole of Ag^+ ions has a mass of 107.9 g. The amount of electricity required to deposit this mass of silver is therefore the Faraday constant (F):

$$F = \frac{107.9}{0.001118} \\ = 96\,500 \text{ C mol}^{-1}$$

This quantity of electricity will therefore discharge or cause to pass into solution $1/z$ mole of any ion, during electrolysis.

EXAMPLE

A current of 1 A was passed for 30 minutes through (a) a cell with platinum electrodes filled with dilute sulphuric acid, in which the hydrogen produced at the cathode by discharge of H^+ ions was collected, and (b) a cell with a copper anode and platinum cathode, filled with a solution of copper(II) sulphate (Cu^{2+} ions discharging at the cathode). What volume of hydrogen at 19°C and 100 kPa will be liberated in (a), and what weight of copper will be deposited on the cathode in (b)?

The quantity of electricity passed is $1 \times 30 \times 60 = 1800 \text{ C}$.

$$(a) \text{ Amount of } \text{H}^+ (z = 1) \text{ discharged} = \frac{1800}{96\,500} \text{ mol}$$

1 mol of H^+ ions will produce $1/2$ mol of H_2 gas,

$$\text{hence amount of hydrogen produced} = \frac{1800}{96\,500 \times 2} \\ = 0.00933 \text{ mol}$$

From the ideal gas equation:

$$V = \frac{nRT}{p} = \frac{0.00933 \times 8.31 \times 292}{10^5} \\ = 2.26 \times 10^{-4} \text{ m}^3 \\ = 226 \text{ cm}^3$$

$$(b) \text{ Amount of } \text{Cu}^{2+} \text{ ions } (z = 2) \text{ discharged} = \frac{1800}{96\,500 \times 2} \\ = 0.00933 \text{ mol}$$

1 mol of copper has a mass of 63.5 g,

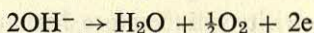
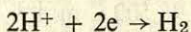
$$\text{hence mass of copper deposited} = 0.00933 \times 63.5 \\ = 0.593 \text{ g}$$

Hence 226 cm^3 of hydrogen were liberated in (a) and 0.593 g of copper deposited in (b).

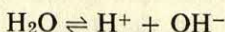
15.6. Examples of electrolysis

Electrolysis of solutions of strong acids, and caustic soda solution

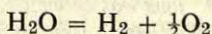
Electrolysis of solutions of most strong acids (*e.g.* sulphuric, nitric) between platinum electrodes yields hydrogen at the cathode and oxygen at the anode; such is the case also with solutions of sodium hydroxide. In all these cases it would appear that the ions discharging are H^+ at the cathode and OH^- at the anode:



The ions that are removed from the solution by electrolysis will be replaced by ionisation of water molecules to maintain the equilibrium



so that the result of the electrolysis is the decomposition of water:



Since the electrode reactions are the same in each case, it is not surprising that the decomposition potentials of all these solutions are practically the same, *i.e.* H_2SO_4 , 1.67 V; HNO_3 , 1.69 V; NaOH , 1.69 V. What requires explanation is why the only ions to discharge are H^+ and OH^- , when the solutions also contain other types of ions (SO_4^{2-} , NO_3^- and Na^+ respectively).

In the case of sulphuric acid (Fig. 99) it will be seen that whereas hydrogen is the only ion that can discharge at the cathode, there are two possibilities at the anode, *i.e.* discharge of either SO_4^{2-} ions or OH^- ions. What is it that decides which process actually occurs? Suppose we imagine the applied e.m.f. to be gradually increased from zero: electrolysis will begin with the process that requires the lowest decomposition potential. The back e.m.f. of the electrolysis cell is equal to $E_{\text{anode}} - E_{\text{cathode}}$, so that the products of electrolysis must be those that give the least *positive* e.m.f. at the anode, and the least *negative*

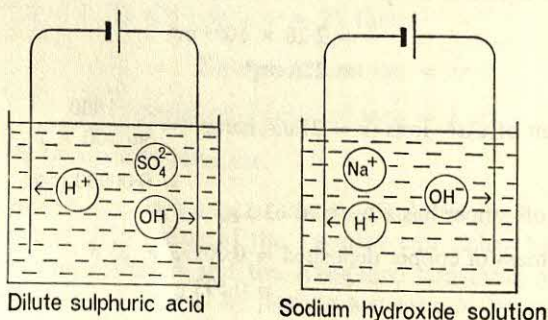


Fig. 99. Electrolysis of solutions between platinum electrodes, showing all the types of ions present and those that discharge at the two electrodes

e.m.f. at the cathode. In the present example, the discharge of OH^- ions requires a much smaller positive potential than does the discharge of SO_4^{2-} ions, so that although the concentration of OH^- is extremely small in acid solution it is only these ions that discharge at the anode.

With sodium hydroxide solution (see Fig. 99), we have to decide whether Na^+ or H^+ ions will discharge at the cathode. Sodium has a much greater negative electrode potential (-2.71 V) than hydrogen, so that it will be the H^+ ions that discharge. Strictly speaking, the concentrations of the ions should also be taken into account in calculating the discharge potentials. Thus for a 1 mol dm^{-3} solution of sodium hydroxide,

$$[\text{Na}^+] = 1 \quad [\text{OH}^-] = 1 \quad [\text{H}^+] = \frac{10^{-14}}{[\text{OH}^-]} = 10^{-14}$$

The e.m.f. of a sodium electrode in this solution would therefore have an electrode potential equal to the standard value (-2.71 V), but the e.m.f. of a hydrogen electrode would be given by the Nernst equation:

$$\begin{aligned} E &= E^\circ + \frac{0.059}{1} \log_{10} 10^{-14} \\ &= 0 - 0.059 \times 14 \\ &= -0.83 \text{ V} \end{aligned}$$

The hydrogen electrode still has the lower negative potential.

Electroplating

Electrolysis can be used to deposit a layer of one metal on to an object made of another metal, and electroplating is the most widely used method of protecting metals from corrosion. The coating can be made extremely thin (less than a thousandth of an inch), and this is an important economic consideration since the metal used for plating may be expensive (e.g. gold, silver, tin, nickel, cadmium or chromium).

The electrolyte in a plating cell will consist of a solution of a salt of the metal to be plated: the positive ions present are therefore the metal ions and hydrogen ions. Examination of the table of electrode potentials will show that gold, silver and copper are more positive than hydrogen, and so will discharge at the cathode (*i.e.* the object to be plated) in preference to hydrogen. The other metals have a more negative potential than hydrogen, and it might be expected that in these cases hydrogen would be evolved and no metal deposited: There is, however, a further factor to be considered, which is the high overpotential of hydrogen at most metal surfaces. This increases the potential required for the evolution of hydrogen. The overpotential can also be increased by using a high current density, so it is possible to deposit metals with a high negative electrode potential, e.g. $\text{Zn}(-0.76 \text{ V})$ which has a hydrogen overpotential of very nearly the same value; and Cr , which has

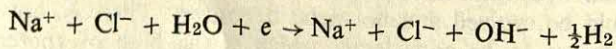
a lower overpotential for hydrogen, but which can be deposited at a high current density. It frequently happens that both processes occur, so that metal is deposited and hydrogen evolved simultaneously.

The anode of a plating cell is usually made of the metal that is being deposited, and during electrolysis metal ions pass into solution from this electrode, thus maintaining the concentration of metal in solution, which would otherwise soon be exhausted. This type of anode reaction has not been considered previously, because in the cells dealt with so far the anode has been of platinum, which has a high positive electrode potential. The dissolution of a metal anode is another type of oxidation reaction that can take place at the anode, as an alternative to the discharge of negative ions. In neutral or acid solution the discharge of OH^- ions (allowing for the concentration term in the Nernst equation) requires an anode potential greater than 0.8 V. Any metal with an electrode potential less than this value will therefore dissolve from the anode in preference to the discharge of OH^- ions. Any other negative ions that are present (*e.g.* Cl^- , SO_4^{2-} , NO_3^-) will be unable to discharge, since they all have higher potentials than the OH^- ion.

The manufacture of caustic soda

It has already been seen that electrolysis of a solution containing sodium ions, between platinum electrodes, causes hydrogen ions, and not sodium, to discharge at the cathode. If, however, there is a mercury cathode, the position is reversed and sodium ions are discharged. This is due (*a*) to the high overpotential of hydrogen at a mercury electrode, and (*b*) to the fact that sodium diffuses into the mercury, so that the concentration at the surface of the electrode is small, thus considerably reducing the potential required for the discharge of sodium ions. In the Kellner-Solvay method, a strong brine solution is electrolysed with a mercury cathode and a carbon anode. The dilute sodium amalgam so formed is then allowed to react with water to give a solution of sodium hydroxide and hydrogen.

Another method of manufacturing caustic soda is the electrolysis of brine between a steel cathode and a carbon anode, the two electrode compartments being separated by means of an asbestos diaphragm (Hooker cell). Hydrogen is liberated at the cathode, and as the hydrogen ions that discharge are provided by the ionisation of water molecules this results in an increase in the concentration of hydroxyl ions in the cathode compartment:



The negative ions are carried by the current towards the anode, thus passing through the diaphragm: since, however, the chloride ions are in large excess, only a small number of hydroxyl ions leave the cathode compartment. The solution in the latter compartment, which contains a mixture of sodium ions, chloride ions and hydroxyl ions, is evaporated.

Sodium chloride is precipitated first, and finally a strong solution of caustic soda is obtained. The chlorine evolved at the anode by discharge of chloride ions is also an important industrial product.

15.7. Measurement of transport numbers by electrolysis

Another characteristic feature of electrolysis is that changes in the concentration of the electrolyte occur near the two electrodes. Consider the electrolysis cell shown in Fig. 100, where an arbitrary volume of electrolyte around the cathode is marked off by a dotted line. If a quantity of electricity equal to the Faraday constant is passed through the cell, it will cause 1 mol of positive ions to discharge at the cathode, so that the portion of electrolyte around the cathode will have lost this amount of positive ions (it is assumed that the ions have a single charge). The current also carries positive ions into this region, but since the positive ion current is only a proportion of the total current (equal to t_+ , the transport number of the positive ion, see § 14.5) the amount carried by 1 Faraday is equal to t_+ mol of ions. There is therefore a net loss of positive ions around the cathode, given by:

$$\begin{aligned}\text{Loss in cathode electrolyte} &= 1 - t_+ \\ &= t_- \text{ mol of positive ions} \\ (\text{since } t_+ + t_- &= 1)\end{aligned}$$

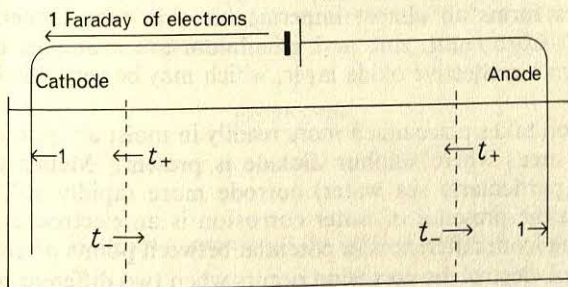


Fig. 100. Concentration changes near the electrodes due to electrolysis

The current will also carry t_- mol of negative ions away from this region, so that the total result is a loss of t_- mol of the electrolyte as a whole.

Transport numbers can be measured by finding the change in concentration, close to the cathode, for a definite quantity of electricity passed:

$$\text{Transport number of anion} = \frac{\text{Loss of electrolyte (mol) from cathode region}}{\text{Quantity of electricity passed (in Faradays)}}$$

If negative ions discharge at the anode, it can be shown that there is a corresponding loss in the region of the anode, equal to the trans-

port number of the cation (t_+) for each Faraday passed. A different situation arises if, instead of discharge of anions, the electrode passes into solution as cations. The anode portion now gains 1 mol of cations per Faraday, and loses t_+ mol, so that there is a net gain of $(1 - t_+) = t_-$ mol.

Transport numbers were first measured in this way by Hittorf, and the apparatus has separate compartments for the two electrodes. After passing a measured quantity of electricity, the electrolyte from one (or both) electrode compartments is run out and analysed to find the net gain or loss.

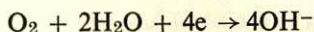
15.8. The corrosion of metals

Metals are subject, in varying degrees, to chemical action with their surroundings. A typical example is the rusting of iron, which takes place in a moist atmosphere by a surface reaction which converts the metal into an oxide. In general, the term *corrosion* is used to describe surface reactions by which metals are converted into chemical compounds.

In dry air at ordinary temperatures most metals tend to oxidise (the exceptions are the so-called "noble" metals, such as gold) but the oxidation does not take place very rapidly. This is due (a) to the fact that the reaction between metals and gaseous oxygen is slow, and (b) to the layer of oxide which forms on the surface of the metal, and which in some cases forms an almost impermeable skin that hinders further oxidation. Chromium, zinc and aluminium are examples of metals which form a protective oxide layer, which may be very thin (10 nm or less).

Corrosion takes place much more readily in moist air, particularly in industrial areas where sulphur dioxide is present. Metals immersed in water (particularly sea water) corrode more rapidly still. This is because in the presence of water corrosion is an electrochemical process, arising from differences in potential between points on the surface. One type of electrolytic corrosion occurs when two different metals are in contact. Consider a junction between two metals, e.g. iron and copper, immersed in a salt solution (Fig. 101). This is equivalent to a chemical cell with the electrodes short-circuited. The copper, having a more positive electrode potential than the iron, will be the positive pole. Electrons will flow from iron to copper through the junction while in the salt solution iron is the anode and copper the cathode.

At the anode, the possible electrode reactions are the discharge of chloride or hydroxyl ions, or the dissolution of iron. The latter has the lowest positive electrode potential, so that the iron near the junction will pass into solution as Fe^{2+} ions. Possible cathode reactions would include the discharge of sodium or hydrogen ions, but there is an alternative reaction which requires a lower negative potential, i.e. the reduction of dissolved oxygen to hydroxyl ions:



The cathode, in fact, behaves as an oxygen electrode, converting the oxygen from the atmosphere into hydroxyl ions. These ions are carried by the electrolytic current towards the anode and combine with the Fe^{2+} ions to form iron(II) hydroxide. The net effect is that the iron near the junction is continuously corroded, while the copper is not affected.

In the above example, it will be seen that it is the metal with the lower electrode potential that corrodes, and this is sometimes expressed by saying that copper is more noble than iron, or that iron is more base than copper. The electrochemical series is not a completely reliable guide as to which of a pair of metals is the more noble, because the concentration of the ions of the metal involved is often quite small when corrosion is taking place, so that the electrode potential may be appreciably different from the standard electrode potential. Aluminium, for example, is more noble than zinc in sea water, although the standard electrode potential is nearly a volt more negative.

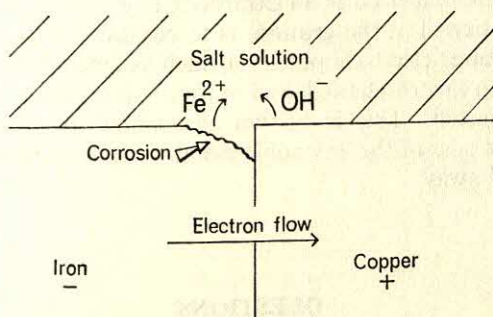


Fig. 101. Electrolytic corrosion at the junction between two metals

Metallic junctions represent the best possible conditions for electrolytic corrosion, and are avoided wherever possible. However, a similar situation arises even with single metals. If there is a break in the oxide film on an iron surface, for example, the exposed iron becomes the anode and the oxide layer the cathode in a small electrolytic cell, and corrosion proceeds by the same process as described above. This happens not only when the metal is immersed in water but also in moist air. In the latter case, a film of water may form on the surface, or the water may be absorbed by the oxide layer.

Several methods are available for reducing or preventing metallic corrosion. The metal may be alloyed with suitable materials which improve the resistance to corrosion; for example, stainless steel

(containing chromium and nickel) has a more effective oxide film than ordinary steel.

Another widely used method is to apply a protective coating, either of paint or a less corrodible metal (gold, silver, copper, tin, nickel, cadmium, chromium, zinc or aluminium). Metal coatings can be applied by dipping the object in the molten metal (e.g. "galvanising" with zinc, and "tinplating"); by spraying (e.g. "sherardising" with zinc, and aluminium spraying); and by electroplating. If a metal coating is imperfect, then in damp conditions an electrolytic cell will be formed at the break in the protecting layer. The situation is then similar to that shown in Fig. 101 and the metal with the lower electrode potential will pass into solution. Hence, it can be concluded that when iron is protected by a plating of tin a gap in the plating will result in corrosion of the iron, since iron has the lower potential. In the case of galvanised iron, on the other hand, the zinc has the lower potential and therefore it is the plating that dissolves.

In all the examples of electrolytic corrosion given above, it will be seen that it is the electrode with the lower potential—*i.e.* the anode of the cell—which dissolves. A useful way of protecting large objects of a corrodible metal immersed in an electrolyte (e.g. the iron hull of a ship, or iron pipes buried in the ground) is to connect them with pieces of metal with a lower electrode potential, such as zinc. The zinc becomes the anode of an electrolytic cell, and in time will dissolve, while the iron object is protected. This is known as *cathodic protection*, and the *sacrificial electrodes* of the less noble metal must be replaced when they have corroded away.

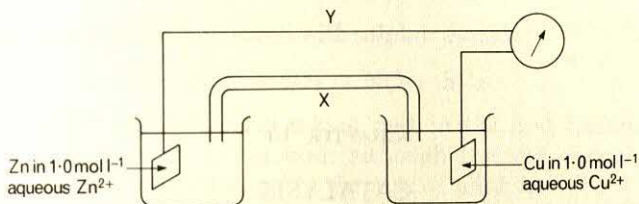
QUESTIONS

G.C.E.

1. Some standard reduction potentials (in volts at 298 K) and the reactions to which they apply are given below:

	$E^\ominus$	Electrode reaction
$\text{Li}^+(\text{aq})/\text{Li}(\text{s})$	-3.04	$\text{Li}^+ + \text{e} \rightleftharpoons \text{Li}$
$\text{Zn}^{2+}(\text{aq})/\text{Zn}(\text{s})$	-0.76	$\text{Zn}^{2+} + 2\text{e} \rightleftharpoons \text{Zn}$
$\text{Cu}^{2+}(\text{aq}), \text{Cu}^+(\text{aq})/\text{Pt}$	0.17	$\text{Cu}^{2+} + \text{e} \rightleftharpoons \text{Cu}^+$
$\text{Cu}^{2+}(\text{aq})/\text{Cu}(\text{s})$	0.34	$\text{Cu}^{2+} + 2\text{e} \rightleftharpoons \text{Cu}$
$\text{I}_2(\text{aq}), 2\text{I}^-(\text{aq})/\text{Pt}$	0.54	$\text{I}_2 + 2\text{e} \rightleftharpoons 2\text{I}^-$
$\text{Fe}^{3+}(\text{aq}), \text{Fe}^{2+}(\text{aq})/\text{Pt}$	0.74	$\text{Fe}^{3+} + \text{e} \rightleftharpoons \text{Fe}^{2+}$
$\text{Ag}^+(\text{aq})/\text{Ag}(\text{s})$	0.80	$\text{Ag}^+ + \text{e} \rightleftharpoons \text{Ag}$

(a) Define *standard reduction potential*. (b) (i) Which is the strongest oxidising agent of all the species given? (ii) Which species in the table can be oxidised by aqueous iodine? (c) The following diagram represents an electrochemical system:



(i) Explain why it is necessary to have **two, separate** vessels joined by a bridge, **X**. (ii) Calculate the e.m.f. of the cell from the data given. (iii) Give the chemical equation for the overall reaction taking place in the cell. (iv) Show the direction of the electron flow in the outer circuit **Y**, and explain why there is electron flow in this direction. [W.J.E.C.]

2. Two voltameters are connected in series, one containing a solution of silver nitrate, the other a solution of copper(II) sulphate. A steady current I is passed through the two voltameters for ten minutes, and 0.54 g of silver are deposited on the cathode of the first voltameter. Calculate (i) the current I , (ii) the mass of copper (to two significant figures) deposited on the cathode of the second voltameter. (Take the Faraday constant to be $96\,000\text{ C mol}^{-1}$.)

[Oxford]

CHAPTER 16

CATALYSIS

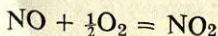
16.1. The nature of catalysis

It has already been stressed that a chemical reaction cannot be of practical use unless it proceeds at a suitable speed. If a reaction is too slow it can be speeded up by raising the temperature, but this may have undesirable results; for example, if the reaction is exothermic the equilibrium constant will decrease, so that the yield of products will be less. However, it is also found that the rates of very many reactions are considerably increased by the presence of quite small amounts of another substance, which is not itself used up during the reaction. This phenomenon is described as *catalysis*, and a *catalyst* is therefore *a substance which increases the rate of a reaction but remains unchanged chemically in the process*.

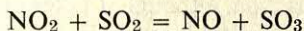
A wide variety of substances can act as catalysts, but a particular type of catalyst is usually effective only for a certain type of reaction. In other words, catalyst action is specific in nature. A common example in the laboratory is the way in which acids and alkalis catalyse the hydrolysis of a large number of organic compounds, *e.g.* esters, amides and nitriles. Solids—particularly metals—can also act as catalysts. One of the earliest known examples of catalysis was the decomposition of hydrogen peroxide when in contact with metal surfaces, while today metal catalysts are used in a large number of gaseous reactions. Another very important class of catalysts controls the speed of reactions taking place in plants and animals; these are the enzymes, which are complex compounds produced by living cells.

Although catalysts may take many forms, they all have the following characteristics:

(a) *The catalyst is unchanged chemically at the end of the reaction.* The amount of catalyst remains the same throughout the reaction, and it is the same chemically at the end of the reaction as it was at the beginning. This does not mean that the catalyst takes no chemical part in the reaction, in fact it is an essential feature of catalysis that it should do so. To understand this apparent contradiction, consider the formation of sulphur trioxide in the lead-chamber process, where sulphur dioxide and air are mixed with oxides of nitrogen. The catalyst is nitrogen oxide, which first reacts with oxygen to form nitrogen dioxide:

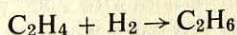


The nitrogen dioxide then reacts with sulphur dioxide:

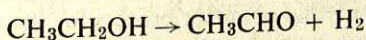


The nitrogen oxide molecule taking part in the first reaction is regenerated by the second reaction: although reacting chemically, the nitrogen oxide is not used up. In the case of solid catalysts, it is quite possible for a physical change to occur. The surface of a metal catalyst often becomes roughened in use, although there is no change in the amount of catalyst or in its chemical constitution. Since the catalyst is not used up, it follows that a very small amount of catalyst may bring about a considerable amount of reaction. When the catalyst is very effective in speeding up the reaction, only a minute quantity may be required; for example, hydrogen peroxide can be decomposed by the presence of colloidal platinum at a concentration of $10^{-8} \text{ mol dm}^{-3}$, or by a very small quantity of the enzyme catalase. However, the rates of catalysed reactions are often proportional to the concentration of catalyst (or to the surface area, if the catalyst is a solid), so that the reaction rate can be increased, where necessary, by using larger amounts of the catalyst.

(b) *The catalyst does not alter the position of equilibrium in a reversible reaction*, in other words the value of the equilibrium constant is the same whether a catalyst is used or not. This arises from the fact that the catalyst is unchanged chemically, so that it does not contribute any additional energy change to the reaction. An interesting deduction can be made about the effect of the catalyst on the rates of the forward and reverse reactions: the equilibrium constant is equal to the ratio of the two rate constants ($K = k_1/k_2$), so that the catalyst must increase the rate constants of both reactions in the same proportion. It follows that a substance that is a good catalyst for the forward reaction must be equally effective in speeding up the reverse reaction. This often applies in a more general sense to particular types of reaction and their reverse, *e.g.* to hydrogenation and dehydrogenation reactions. Nickel can act as catalyst for both of these, *e.g.* in the hydrogenation of an unsaturated hydrocarbon



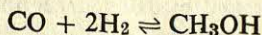
and the dehydrogenation of an alcohol to an aldehyde



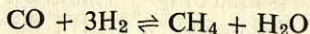
(c) *The catalyst does not initiate a reaction that would not otherwise occur*. Many reactions occur when a catalyst is present that do not appear to take place at all by themselves. Combustion reactions illustrate this fact. For example, hydrogen does not appear to react with oxygen at room temperature, nor do gaseous hydrocarbons (*e.g.* methane), but these reactions proceed readily in the presence of a suitable catalyst such as platinum. It might be argued that, in the

absence of the catalyst, no reaction is occurring, but it is much more likely that there is a reaction, although it takes place so slowly as to be undetectable. One piece of evidence which supports this view is that combustion reactions do take place at a measurable rate, at higher temperatures, without a catalyst. The statement that catalysts never initiate reactions is in the nature of a proposition, which cannot be proved by experiment but is very likely to be true.

Most chemical reactions are complex, *i.e.* they take place in a number of steps, and there are often alternative paths which may produce different products. The reaction that predominates is the one with the lowest activation energy. When a catalyst is used, it may increase the rate of a process that was previously immeasurably slow, in which case the products of the catalysed reaction may differ from those of the uncatalysed reaction. In the same way, different catalysts may give quite different products: for example, water gas (a mixture of carbon monoxide and hydrogen) is partly converted into methanol when passed over a catalyst of zinc and chromium oxides at 400°C:



whereas nickel at the same temperature causes the formation of methane:

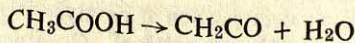


It must be emphasised that the catalyst does not alter the nature of the products of the reaction which it accelerates, but different catalysts may affect the rates of different alternative processes.

Some examples of catalysis will now be considered in more detail. It is convenient to deal separately with *homogeneous catalysis*, where the catalyst and reactants are in the same phase (*i.e.* the system may consist entirely of gases, or both catalyst and reactants may be in solution); and *heterogeneous catalysis*, where the catalyst is usually a solid and the reactants are in a different phase (either liquid or gas).

16.2. Homogeneous catalysis

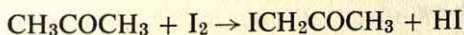
There are comparatively few cases where gaseous reactions are catalysed by gaseous catalysts. One example which has already been mentioned is the combination of sulphur dioxide and oxygen, catalysed by nitrogen oxide, in the lead-chamber process for the manufacture of sulphuric acid. Another example is the decomposition of ethanoic acid to ketene at 650°C, catalysed by triethyl phosphate:



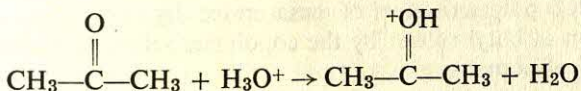
Homogeneous catalysis in solution is much more common, the most important class of such reactions being those that are catalysed by the presence of acids and bases, *i.e.* *acid-base catalysis*. One example is the hydrolysis of esters, *e.g.* methyl ethanoate:



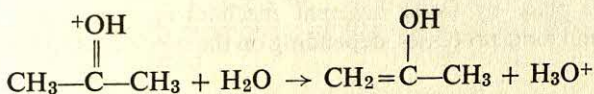
This reaction by itself proceeds very slowly, but it is greatly accelerated in the presence of hydrogen ions (supplied by a strong acid, *e.g.* hydrochloric) or hydroxyl ions (from sodium hydroxide). Many other organic reactions, including some hydrolysis reactions, are found to be catalysed by *any* acid or base as defined in terms of the proton transfer theory (see § 14.6). Acids (proton donors) will therefore include the hydrogen ion, weak acids, the cations of salts of weak bases, and water; while bases (proton acceptors) can be hydroxyl ions, weak bases, the anions of salts of weak acids, or water. It is evident that acid-base catalysis must take place by a proton transfer mechanism. An example of the way in which this may occur can be seen from the reaction between propanone and iodine,



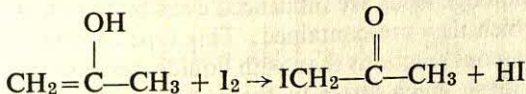
which is catalysed by acids and bases. The probable mechanism is as follows. If a strong acid is present, the catalyst will be the hydrogen ion (H_3O^+) which will donate a proton to the propanone:



The propanone molecule plus the proton will now be acidic, *i.e.* it will have a tendency to lose its proton by transferring it to a base. In a strong acid solution the water is the only substance that has basic properties, so that a water molecule will accept the proton:



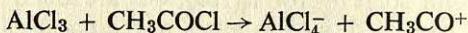
It will be seen that the hydrogen has been removed from a different position in the molecule, so that the latter is now in what is called the *enol* form and can readily react with iodine:



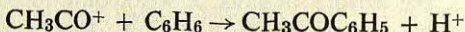
Two points should be especially noted: first, the reaction has been made easier (and therefore quicker) as a result of the addition of a proton to the propanone molecule and its subsequent removal; second, it is necessary for *both an acid and a base to be present* for this type of catalysis to take place. Water can act either as an acid, in conjunction with a strong base, or as a base in conjunction with a strong acid.

The Friedel-Crafts reaction illustrates a different type of catalysis which, although also proceeding by an ionic mechanism, takes place in

non-aqueous solution with anhydrous aluminium chloride as the catalyst. The aluminium chloride acts as an electron acceptor, and is thought to remove a chloride ion from an organic chloride, leaving the remainder of the molecule charged. With ethanoyl chloride, for example:



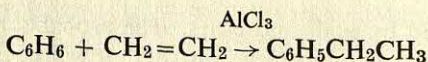
The ethanoyl ion can then react with a hydrocarbon, *e.g.* benzene:



Finally



An industrial example of the Friedel-Crafts reaction is the production of ethylbenzene (an intermediate in the manufacture of styrene) from benzene and ethene:



Aluminium chloride and similar metal halides (*e.g.* TiCl_4 , BF_3) can also catalyse the polymerisation of unsaturated hydrocarbons, as in the production of butyl rubber by the copolymerisation of isobutene with about 2% of isoprene.

Catalysis plays a large part in many different types of polymerisation reactions. Reactions of the condensation type, *e.g.* when a diacid and a glycol combine to form a polyester, are acid-base catalysed in the same way as the reaction of an alcohol and an acid to form an ester. The polymerisation of unsaturated hydrocarbons (*e.g.* ethene, styrene) can take place by many different mechanisms, including both free radical and ionic processes, depending on the type of catalyst used.

16.3. Heterogeneous catalysis

The rates of many chemical reactions are greatly increased by solid catalysts, in fact it has been found that some reactions previously thought to be homogeneous are influenced even by the glass surface of the vessel in which they are contained. This type of catalysis is more effective with gaseous reactions than with liquids, because the molecules in a gas can diffuse much faster to the surface of the solid, and the gaseous products can also diffuse more readily away from the surface. Very many industrial reactions are now carried out by heterogeneous catalysis, including such important examples as the Haber process for the production of ammonia, the contact process for sulphuric acid, the Bosch process for hydrogen, the refining of petroleum, and the synthesis of alcohols, aldehydes, phenol, butadiene, styrene, vinyl chloride and many other important organic compounds.

Among the many different materials used as catalysts are the metals

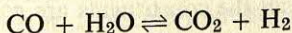
nickel, iron, copper, platinum and silver; oxides of iron, aluminium, and chromium; chlorides of aluminium, titanium and mercury; and phosphoric acid. Solid catalysts are carefully prepared so as to ensure a clean surface and a large surface area and some are supported on a porous material such as kieselguhr or charcoal. It is found that the effectiveness of many catalysts is increased by the incorporation of small amounts of substances known as promoters, which include the oxides of aluminium, zirconium, magnesium, silicon and potassium.

Heterogeneous catalysis is very well suited to continuous industrial processes. The gaseous reactants are passed through a reaction zone containing the catalyst and maintained at the desired temperature. The catalyst may be fixed, or it may be in the form of a *fluidised bed*. In the latter, the catalyst is in the form of small particles of uniform size, and the gas stream passes upwards through the bed, causing the particles to be suspended in the gas stream and to move about freely: their weight prevents them being carried away by the gas. A fluidised bed has certain practical advantages in that it allows more effective contact between the gases and catalyst and also causes a much more efficient heat exchange between the wall of the reaction chamber and the reacting system, which is a great advantage when the reaction absorbs or evolves large amounts of heat.

The following are some of the more important examples of heterogeneous catalysis.

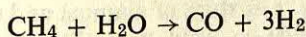
The manufacture of hydrogen

In the Bosch process, water gas (a mixture of carbon monoxide and hydrogen) is mixed with excess of steam and passed over a catalyst consisting of iron with promoters, at 400–450°C, when carbon dioxide and hydrogen are formed:



The carbon dioxide is dissolved out by water, under pressure.

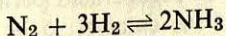
Another method is the reaction between methane and steam, using a nickel catalyst at 750–900°C:



This is used where natural gas is available.

The Haber process for ammonia

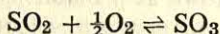
Nitrogen and hydrogen in the correct molecular proportion are used, and an iron catalyst with oxide promoters. The gases are at high pressure, to increase the yield of ammonia (see § 13.4), and a temperature of about 450°C.



As the yield of ammonia is only about 25–75% (depending on the pressure), the ammonia is condensed out by refrigeration and the gases recirculated.

The contact process for sulphuric acid

The essential part of this process is the oxidation of sulphur dioxide



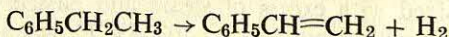
Platinum was originally used to catalyse this reaction, but now vanadium(V) oxide on kieselguhr is used, with a considerable saving in cost. Temperatures up to 600°C are employed.

Hydrogenation and dehydrogenation

It has already been explained that a catalyst that is effective for one type of reaction also catalyses the reverse reaction. Thus nickel can be used for both hydrogenation and dehydrogenation reactions, as also can chromic oxide.

An example of hydrogenation is the hardening of vegetable oils for the manufacture of margarine. The oils consist of esters of glycerol with fatty acids, some of the acids being unsaturated. The oils and low-melting fats are converted into higher-melting fats by partial hydrogenation in the presence of a nickel catalyst. The oil is mixed with finely-divided nickel (or nickel supported on kieselguhr) and heated to 180–200°C, hydrogen being blown in at a pressure of 200–500 kPa.

Styrene (from which the thermoplastic polystyrene is made) is produced by the dehydrogenation of ethylbenzene:



This reaction is carried out over a mixture of metal oxides at 600°C, at which temperature all the constituents are gaseous.

The cracking of petroleum

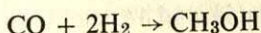
Petroleum, which consists mainly of saturated paraffin hydrocarbons, is broken down into smaller molecules under the influence of heat and a suitable catalyst (*e.g.* a mixture of alumina and silica). By this means heavy oils can be made to yield “petrol” for cars and aeroplanes; petroleum spirit can also be broken down into the smaller olefine hydrocarbons ethene, propene and butadiene. The latter process is now the major source of a large number of important chemicals, many of which are also made by processes involving heterogeneous catalysis.

In the cracking process the petroleum is vaporised at about 500°C and passed through a fluidised bed of the catalyst. During the reaction, carbon is deposited on the surface of the catalyst, thus reducing its activity, so that it has to be regenerated periodically. This is done by allowing a proportion of the catalyst to be carried on with the gas

stream, from which it is later separated, heated to a high temperature to burn off the carbon and then returned to the catalyst bed.

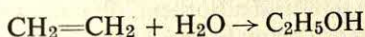
The manufacture of methanol

Methanol is made by passing carbon monoxide and hydrogen over a catalyst of mixed zinc and chromium oxides with promoters, at a high pressure (2×10^7 Pa) and at a temperature of 400°C :



The manufacture of ethanol

Ethene (from petroleum) is mixed with steam at 300°C and a pressure of 7×10^6 Pa, and the mixture is passed over phosphoric acid on a solid support:



When the mixture is cooled, a dilute solution of ethanol in water is obtained.

16.4. The mechanism of heterogeneous catalysis

Some of the examples of homogeneous catalysis given in § 16.2 showed how the catalyst combines with the reactant molecule to form an intermediate, thus offering an alternative path for the reaction to take. Heterogeneous catalysis works in the same way, but in this case it is the surface of the solid catalyst with which the reacting molecule must combine. To understand why this occurs it is useful to examine what happens when a solid surface is exposed to a gas.

It is now known that all solids in contact with a gas accumulate a film of gas molecules on the surface. The forces that cause the molecules to adhere to the surface may be either (a) the normal forces of attraction between molecules (van der Waals forces), or (b) chemical bonds formed between the molecule and the surface. This phenomenon is known as *adsorption* and it must not be confused with *absorption*, which refers to one material passing *into* another. Gases can be *absorbed* by liquids and (in some cases) by solids; for example, palladium can absorb considerable amounts of hydrogen: what is produced here is a solution of the gas in the solid. *Adsorption* takes place only on the surface, and produces a high surface concentration of the adsorbed substance as shown in Fig. 102.

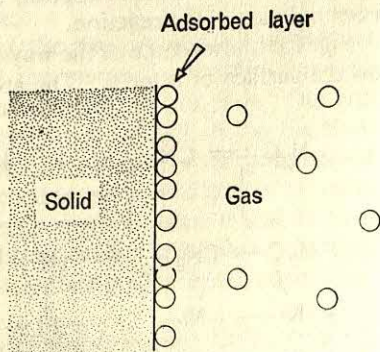


Fig. 102. Adsorption of a gas on a solid surface

The type of force that holds the adsorbed molecule on the surface has a considerable effect on certain characteristics, in particular how tightly the molecules are held and whether the solid will adsorb certain substances more strongly than others. For this reason two types of adsorption are recognised.

In *physical adsorption* the molecules are held by the forces of intermolecular attraction. The process of adsorption is similar to the condensation of gas to liquid, and an equilibrium is established between the rate at which molecules are adsorbed and the rate at which they leave the surface again. On raising the temperature, the increase in kinetic energy causes molecules to leave the surface more rapidly, and the amount that is adsorbed decreases. If different gases are present, those with lower boiling points will be adsorbed to a greater extent. Charcoal, which is a powerful adsorbent, illustrates this point very well. It can be used to remove many harmful vapours from air (as in respirators for protection against toxic gases) but is ineffective in dealing with carbon monoxide, which has a low boiling point. Physical adsorption is independent of the chemical nature of the substance being adsorbed, so that it is unlikely that it plays any appreciable part in catalysis.

Adsorption by chemical forces is known as *chemisorption*, and here there is a chemical bond formed between the adsorbed molecule and the surface. This means that chemisorption is highly selective, since only certain types of molecule will be adsorbed by a particular solid. Hydrogen is strongly adsorbed by the metals nickel, iron and platinum, and by certain metal oxides: these materials are found to be good catalysts for hydrogenation and dehydrogenation. Alumina, which catalyses dehydration reactions, adsorbs water. Platinum and tungsten adsorb oxygen, and catalyse oxidation reactions. In these cases there is an obvious connection between the type of molecule that is strongly adsorbed and the chemical reactions which the solid will catalyse. Some types of heterogeneous catalysis are not yet fully understood, but it is probable that chemisorption of at least one of the reactants is an essential part of the reaction.

Fig. 103 shows some of the ways in which molecules can be adsorbed on the surface of a metal. The atoms at the surface of the solid have

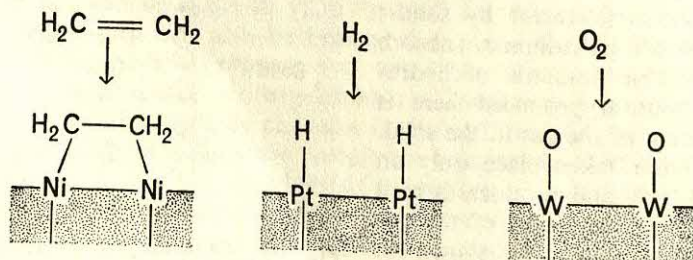
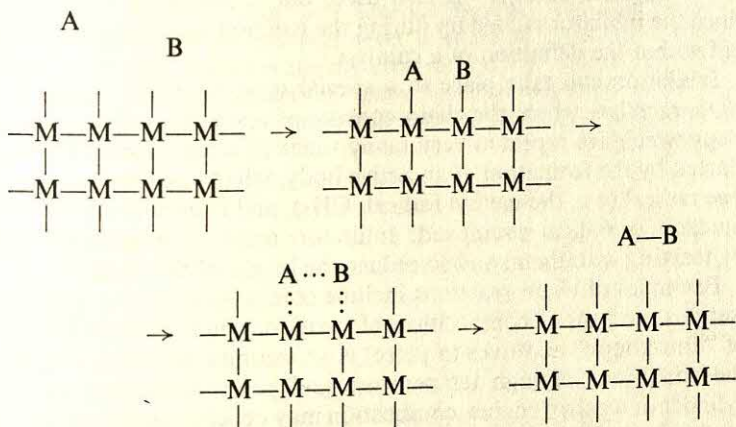


Fig. 103. Chemisorption

unsatisfied valencies which can form chemical bonds with the adsorbed molecules, but this necessitates a change in the bond structure of the molecules. With an ethene molecule, for example, the double bond can open to provide two bonds with the surface. Hydrogen and oxygen, on the other hand, dissociate so that they are adsorbed as single atoms. The result of adsorption is to make the molecules more chemically reactive than they are in the normal state, in other words the reactions in which they take part will have a lower activation energy than the same reactions between normal molecules. A reaction taking place on the surface of a solid catalyst can therefore be very much faster than it would be between molecules in the gas (or liquid) phase.

Where there are two reactants, reaction may occur by adsorption of two molecules adjacent to one another, followed by the formation of an intermediate complex and finally the desorption of the products:



In other cases one reactant may be adsorbed in the atomic state, in which case the second molecule probably attaches itself to the adsorbed atom rather than to the metal surface.

It is desirable that the products of the reaction should be able to leave the surface quickly, otherwise the amount of surface free for further reaction becomes restricted and the reaction rate falls. This can be regarded as *poisoning* of the catalyst by a product of the reaction. A more serious type of poisoning can be caused by the presence of strongly adsorbed impurities in the reacting gases, and failure of metal catalysts to maintain their activity has sometimes been traced to very small amounts of readily adsorbed substances such as sulphur or arsenic compounds, which cover the catalyst surface and prevent adsorption of the reactants.

It has been found that the amount of a poison required to stop the reaction completely is less than the theoretical quantity needed to cover the whole of the surface, assuming a unimolecular layer to be formed.

This indicates that catalytic activity is confined to a comparatively small area of the surface, and it is now recognised that reaction takes place at certain points on the surface known as *active centres*.

The increase in catalytic activity caused by promoters has not yet been fully explained, but it is probably due to a combination of several different factors. Alteration of the spacing in the crystal lattice is thought to be important, since an adsorbed molecule may be attached to two points on the surface and this would require the active points to be the correct distance apart to fit the dimensions of the adsorbed molecule.

16.5. Inhibition

The rates of some reactions are reduced by the presence of small amounts of other substances; the latter are known as *inhibitors*. The term "negative catalyst" is also used, but is not to be recommended since the inhibitor is used up during the reaction and therefore does not fall within the definition of a catalyst.

Inhibition can take place in a special type of reaction known as a *chain reaction*, where the chain consists of a small number of reaction steps which are repeated very many times at a fast rate. The chain is started by the formation of an active body, which is either an atom or a free radical (e.g. the methyl radical, CH_3), and is only terminated when the atom or radical is removed. Inhibitors remove the atoms or radicals by reacting with them, and so reduce the length of the chains.

Examples of chain reactions include combustion reactions, polymerisations, and the decomposition of many organic molecules. The use of "anti-knock" additives to petrol is an example of inhibition. Under the conditions of high temperature and pressure existing inside the cylinder of a petrol engine, combustion may occur spontaneously, ahead of the flame initiated by the sparking plug, and cause "knock". The addition of a volatile lead compound (e.g. lead tetraethyl) inhibits the reaction and prevents this.

QUESTIONS

G.C.E.

1. What are the essential characteristics of a catalytic change? Under what conditions is the use of a catalyst advantageous? Illustrate your answer by reference, in some detail, to the use of catalysts (a) in laboratory experiments, (b) in industrial processes. [London, "S"]

2. State THREE characteristic features of catalytic action. Outline ONE manufacturing process in EACH case in which the following are used as catalysts: (a) nickel, (b) iron, (c) vanadium pentoxide. [Cambridge]

3. The reaction between iodine and propanone (acetone) in aqueous solu-

tion, $\text{CH}_3\text{COCH}_3 + \text{I}_2 = \text{CH}_2\text{ICOCH}_3 + \text{HI}$, is catalysed by hydrogen ions.

(a) Describe briefly the experiments you would perform to determine the order of the reaction with respect to iodine, to propanone and to hydrogen ions. (b) It is found that the rate of this reaction is proportional to the first power of the propanone concentration and to the first power of the hydrogen ion concentration, but is independent of the iodine concentration. What can you deduce from this? (c) Explain why the usual effect of an increase of temperature on a reaction is to increase the rate at which it takes place.

[Oxford]

4. Explain the meaning of the terms (a) *rate (velocity) constant*, (b) *order of reaction*. How is a knowledge of the order of a reaction useful to the chemist?

The reaction between propanone (acetone) and iodine in acidic solution is first order with respect to both propanone and hydrogen ion and zero order with respect to iodine. Write a rate equation for the reaction and describe in outline how you would attempt to verify this statement.

Explain the following observations as fully as you can. (i) When a piece of silver wire is added to 2 mol dm^{-3} aqueous hydrogen peroxide, oxygen is slowly evolved but, when colloidal silver is added to 2 mol dm^{-3} aqueous hydrogen peroxide, oxygen is rapidly evolved. (ii) The rate of the reaction between potassium manganate(VII) (potassium permanganate) and ethanedioic acid (oxalic acid) in sulphuric acid solution gradually increases at first and then decreases.

[Cambridge]

CHAPTER 17

COLLOIDS

17.1. The nature of colloids

If a solution of iron(III) chloride is poured into boiling water, a clear deep-brown liquid is obtained. The change in colour shows that a chemical reaction has occurred, in fact hydrated iron(III) oxide (often incorrectly described as iron(III) hydroxide) has been formed. The latter is practically insoluble in water and would normally precipitate, but if formed under the right conditions it may remain dispersed throughout the liquid in the form of very small particles. The presence of these particles is shown (in this case) by the colour, but they are not large enough to cause the liquid to appear cloudy. If not too concentrated, the system is quite stable and can be kept for a long time without any precipitation of solid. This is an example of a *colloidal* system. Such systems have certain characteristic properties, which are closely connected with the size of the dispersed particles.

In an ordinary solution, the solute is dispersed throughout the solvent in the form of single molecules or ions, which will be very similar in size to the molecules of the solvent. Most molecules fall within the size range 0.1 to 1 nm. If, on the other hand, an insoluble powder is shaken up with a liquid, the smaller particles may remain distributed throughout the liquid for a time in the form of a *suspension* but will slowly settle out again. Colloidal particles are intermediate in size between normal molecules and matter in suspension, and fall roughly in the range 1 nm to 1 μm . These limits are only approximate, since there is no definite dividing line between a molecular solution and a colloidal dispersion, nor between a colloidal dispersion and a suspension.

Many different types of substance exhibit colloidal behaviour and it is the particle size that is the common factor. Colloidal behaviour can be connected with the greatly increased surface area, compared with the volume, as the size is reduced. The following figures show the relative surface area of the same quantity of material, in spherical particles of different sizes.

Diameter of particles	1 cm	1 μm	1 nm
Relative surface area	1	10 000	10 000 000

The very large surface area of matter in colloidal-size particles means that characteristic properties of surfaces, e.g. adsorption, play an important part.

There are two ways in which colloidal-size particles may arise: (a)

they may consist of aggregates of large numbers of small molecules, as when a material is broken down into small pieces; or (b) they may be single molecules of a substance of very high relative molecular mass, such as starch, proteins, rubber and man-made polymers. The material that is dispersed in the form of particles is called the *disperse phase*, while the material in which it is dispersed is the *dispersion medium*. Colloidal systems are not restricted to dispersions of solid in liquid, in fact either component may be in the form of a gas, liquid or solid (with the one exception that they cannot both be gases, since a gas has no surface). Some of the more common systems are listed in Table 14.

TABLE 14. EXAMPLES OF COLLOIDAL SYSTEMS

<i>Disperse phase</i>	<i>Dispersion medium</i>	<i>Type of system</i>
gas	liquid	foam
liquid	gas	mist
liquid	liquid	emulsion
solid	gas	smoke
solid	liquid	{sol colloidal solution

A common type of system which has not been included in the table is the *gel* (such as the ordinary table jelly and silica gel). Gels are colloidal, and contain both solid and liquid phases, but since both phases are continuous it is difficult to fit such a system into the general classification.

The systems that will be dealt with here in detail are the solid-liquid type, *i.e.* *sols*, or *colloidal solutions*.

17.2. The preparation of lyophobic sols

Such sols are dispersions, usually in water, of a material that is water-insoluble (*e.g.* metals, oxides, sulphides, silver halides, sulphur, silica). Such materials are said to be *lyophobic* (solvent hating). To prepare a sol, it is necessary to disperse the solid in particles of the correct colloidal size, which can be done either (a) by breaking down the bulk material (*dispersion*), or (b) by building up the particles from single molecules (*aggregation*).

Dispersion methods

Mechanical grinding can be used to break the material down to the correct size, as in a "colloid mill" where the solid and dispersion medium are fed between grinding surfaces, usually concentric cones rotating with a very small gap between them. Grinding in an agate mortar may also be effective.

Metals can often be dispersed by forming an electrical arc under

water between electrodes of the metal. The metal is vaporised in the heat of the arc, and the vapour condenses into particles of colloidal size. This method was first used by Bredig to prepare sols of platinum and gold.

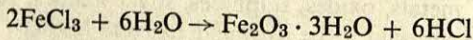
Ionic solids, in the presence of water containing a small concentration of a common ion, tend to break up spontaneously into colloidal particles, a process known as *peptisation*. A precipitate of silver iodide can be peptised by shaking with a dilute solution of either potassium iodide (I^- being the common ion) or silver nitrate (Ag^+). Peptisation is often troublesome in gravimetric analysis, for if some precipitates are washed too thoroughly they will peptise spontaneously and pass through the filter paper. The reason why this does not happen until nearly all electrolytes have been washed out is that sol particles are not stable in the presence of too high a concentration of electrolyte (*see* § 17.5).

Aggregation methods

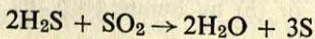
The first step in producing sol particles by aggregation is to prepare a supersaturated solution. The supersaturation will be relieved by crystallisation of the material, and if the conditions are carefully controlled a large number of small crystals can be produced which, by the time all the material has crystallised, have only grown to colloidal size. This can be achieved (*a*) by adjusting the temperature to a value which gives the maximum rate of formation of new crystals and (*b*) having only a small concentration of the disperse phase. Most sols contain less than 1% of dispersed solid. A supersaturated solution can be formed in a number of ways, as shown by the following examples.

Chemical reaction

Hydrolysis can be used to produce hydrated oxide sols of iron, aluminium, chromium and other metals. The preparation of an iron(III) oxide sol by pouring a solution of iron(III) chloride into a large volume of boiling water has already been referred to, the reaction being:



Oxidation. If solutions of hydrogen sulphide and sulphur dioxide are mixed, a sulphur sol is produced:

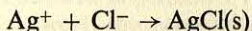


Colloidal sulphur can be formed in qualitative analysis if oxidising agents are present when hydrogen sulphide is used to precipitate metal sulphides. It is then difficult to remove the sulphur, since, although the larger particles will precipitate, those of colloidal size cannot be removed even by centrifuging.

Reduction has been used to prepare sols of several metals, *e.g.* gold, silver and platinum. An example is the preparation of gold sol by the reduction of a solution of gold chloride with white phosphorus.

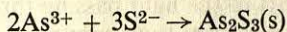
*Ionic equilibria**

If silver nitrate solution is added to a very dilute solution of a chloride, a silver chloride sol is produced:



There must only be a slight excess of either Ag^+ or Cl^- ions. This sol is often observed when testing a solution for the presence of chloride: if only a trace of chloride is present, the solution becomes slightly cloudy but no precipitate forms.

An arsenic(III) sulphide sol is obtained by mixing solutions of hydrogen sulphide and arsenic(III) oxide:

*Change of solvent*

Sulphur is slightly soluble in ethanol, but practically insoluble in water. A saturated solution of sulphur in ethanol, when poured into water, forms a sulphur sol owing to the decrease in solubility. The solvent used must be miscible with water.

17.3. Purification of sols

When a sol has been prepared, there are often other materials left in solution besides the colloidal particles; for example, in an iron(III) oxide sol made by the method described above, hydrochloric acid is also present. It is often desirable to remove these impurities, particularly when they are electrolytes, because these reduce the stability of the sol. Separation can be achieved by taking advantage of the difference in size between dissolved molecules or ions, and the colloidal particles. In the method known as *dialysis* (first used by Graham) the sol is placed inside a membrane, outside which there is pure water (see Fig. 104). The membrane material must be chosen so that small molecules can diffuse readily through it, while the larger colloidal particles, which diffuse much less slowly, are retained. Cellophane or parchment are suitable materials. The water is either changed periodically, or may be arranged to flow continuously past the membrane.

It should be noted that colloids pass through ordinary filter paper, because the pores are too large to retain the particles. It is possible to purify colloids by filtration through membranes with smaller pores, made of collodion or cellophane, and this is known as

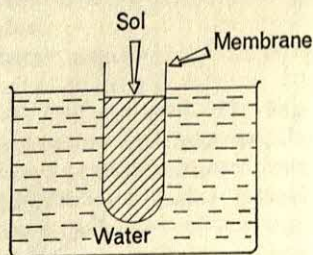


Fig. 104. Dialysis

* The reactions given here are often incorrectly described as "double decompositions": in fact, there is no chemical change involved.

ultrafiltration. It is a slow process, and pressure is applied to the sol to force the liquid, together with the dissolved impurities, through the filter, while the sol particles are retained.

17.4. Properties of lyophobic sols

Sols exhibit characteristic *optical properties*. A beam of light passing through a sol becomes visible, just as a beam of sunlight is seen as it passes through dust-laden air. This is known as the *Tyndall effect*, after its discoverer, and is one way by which the presence of colloidal particles can be demonstrated. Particles of the colloidal size range are too small to be seen, even with a microscope, but they are large enough to scatter light, so that part of the light passing through a sol is scattered at all angles. If the particles are large enough, the sol may even appear turbid in ordinary illumination. Many sols are coloured, showing that light of certain wavelengths is absorbed. This is also connected with the size of the particles, as shown by the case of gold sols, which may be red or blue depending on the particle size.

Information about the shape of colloidal particles has also been obtained by studying light scattering, and this has disclosed that while the particles in some sols are spherical, in others they are in the shape of rods or plates.

The Tyndall effect can also be used to find the position of a colloidal particle. It is not possible to see the particle itself with an ordinary microscope, because the particle is smaller than the wavelength of light. It is, however, possible to observe where the particle is by means of the light that it scatters. In the *ultramicroscope* (Fig. 105) an intense beam of light is passed through the sol, and the scattered light is observed through a microscope arranged at right angles to the beam. The position of individual particles can be seen as spots or flashes of light in the field of the microscope. The particles are found to be in constant motion owing to bombardment by the very fast-moving molecules of the liquid; this is known as the *Brownian movement*.

Other properties of sols are *electrical*: all lyophobic sol particles are

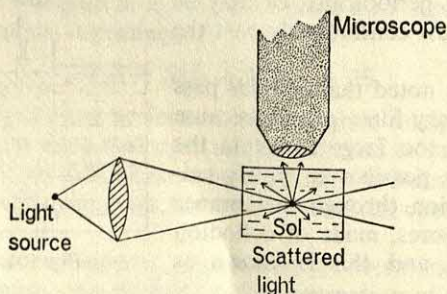


Fig. 105. The ultramicroscope technique for "seeing" a colloidal particle

found to be electrically charged, and the particles in a particular sol all have the same sign. This can be demonstrated by applying an electric field and observing the motion of the particles by means of the ultra-microscope (Fig. 106). The field is obtained by applying a potential difference (about 100 V) between the two electrodes, which will cause positively charged particles to move towards the negative electrode and vice versa. The movement of charged colloidal particles under the influence of an electric field is known as *electrophoresis*.

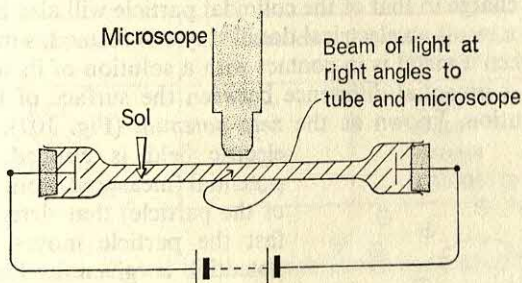


Fig. 106. Electrophoresis, using the ultramicroscope to follow the motion of the particles

With an iron(III) oxide sol, such an experiment shows that all the particles move towards the negative electrode, showing that all the particles carry a positive charge. With an arsenic(III) sulphide sol the movement is in the opposite direction, since this is a negatively charged sol. A particular type of particle does not necessarily always carry a charge of the same sign, as it often depends on the way in which the sol has been prepared. A silver chloride sol made by adding silver nitrate solution to a solution of a chloride, there being a slight excess of chloride ions, is negatively charged; but if a slight excess of silver nitrate is now added the sol becomes positive. Electrophoresis experiments have established the fact that the particles in a stable sol always carry a charge—in fact without this charge the stability is lost.

The question now arises, how is the charge acquired? It has been found that some sols become unstable after continued dialysis, *i.e.* when all electrolytes present in solution have been removed. This suggests that the charge is due to the adsorption of ions from solution, the surface of the particle becoming covered with a layer of adsorbed ions. For this to produce a net charge, it is necessary for the particle to adsorb selectively one type of ion, so that it acquires the charge of that particular ion. In an iron(III) oxide sol, prepared as described above, there is an excess of Fe^{3+} ions in the solution and they are selectively adsorbed to produce positively charged particles; but if the conditions are changed so that there is an excess of OH^- ions, then these are adsorbed and the

sol is negative. An arsenic sulphide sol is negative owing to adsorption of S^{2-} ions. Particles of ionic solids (e.g. silver chloride) will adsorb either of the common ions (Ag^+ or Cl^-) and the charge depends on which ion remains in excess when the sol is formed: if exactly equivalent amounts of silver and chloride ions are mixed in solution, this selective adsorption cannot take place, and a stable sol is not formed.

The charged sol particles have a strong electrical attraction for the polar water molecules, and are therefore hydrated, probably having a complete envelope of water molecules. Any ions in solution that have an opposite charge to that of the colloidal particle will also be attracted by it and as a result an electrical double layer is formed, similar to that produced when a metal is in contact with a solution of its ions. There is therefore a potential difference between the surface of the particle and the solution, known as the *zeta potential* (Fig. 107). When an

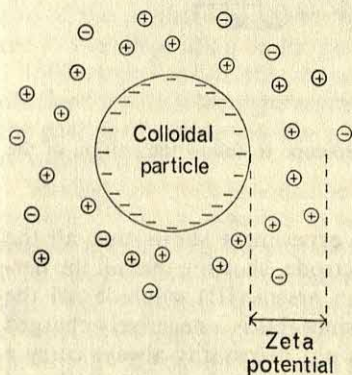


Fig. 107. The electrical double layer around a colloidal particle, and the zeta potential

electric field is applied, it is this potential (measured from the *surface* of the particle) that determines how fast the particle moves. The zeta potential is given a special name to distinguish it from the electrode potential used in chemical cells, which is measured from *inside* the solid.

It is the presence of the electrical double layer that gives sol particles their stability. If there were no electrical charge, then when two particles approached each other the forces of intermolecular attraction would cause them to coalesce, and the particles would continue to grow in size until they precipitated. When, however, the particles have charges

of the same sign, there is a strong electrical repulsive force which keeps them apart and prevents coagulation. This can be demonstrated by mixing a positive sol with a negative sol, when the particles of opposite sign are attracted to each other and coalesce, so that coagulation occurs.

17.5. Coagulations of lyophobic sols by electrolytes

Since the sol particles acquire their charge by adsorbing ions from solution, a stable sol cannot be formed unless there are ions for the particles to adsorb, but the electrolyte concentration required is quite small. If larger amounts of electrolyte are added, coagulation (*i.e.* precipitation) results. Coagulation is a sign of the weakening of the repulsive force due to the electrical charge, so that the forces of attraction become dominant and cause the particles to adhere to one another. When a large amount of electrolyte is added to a sol, the dispersed solid

will be precipitated in a short time. With smaller electrolyte concentrations, coagulation is slower, first becoming noticeable by the appearance of turbidity. For any particular sol there are certain minimum concentrations of different electrolytes that will cause coagulation: Table 15 shows some figures obtained with a negatively charged arsenic sulphide sol. It will be seen that BaCl_2 is much more effective than either of the

TABLE 15. CONCENTRATIONS OF ELECTROLYTE REQUIRED TO COAGULATE A NEGATIVELY CHARGED ARSENIC SULPHIDE SOL

<i>Electrolyte</i>	<i>Positive ion</i>	<i>Concentration</i> (mol dm ⁻³)
KCl	K ⁺	0.050
K ₂ SO ₄	K ⁺	0.066
BaCl ₂	Ba ²⁺	0.00069
Al(NO ₃) ₃	Al ³⁺	0.000095

potassium salts (as shown by the much lower concentration needed), while $\text{Al}(\text{NO}_3)_3$ is more effective still. This indicates that it is the positive ions that cause coagulation in this case, since the increase in coagulating power can then be explained by the increase in the charge on these ions in the order $\text{K}^+ \rightarrow \text{Ba}^{2+} \rightarrow \text{Al}^{3+}$. The negative ions do not appear to have much influence, since KCl and K_2SO_4 (with singly and doubly charged negative ions respectively) are effective in very similar concentrations.

Experiments with positively charged sols show that in that case it is the negative ions which cause coagulation. The results of such experiments are summarised in the *Schulze-Hardy rule*, which states that *coagulation is caused by the ion whose charge is of opposite sign to that of the colloidal particle, and the coagulating power of an ion increases rapidly with the magnitude of its charge.*

It can now be seen why it is desirable to remove electrolytes from freshly prepared sols by dialysis. The electrolyte concentration need only be reduced to below the point where coagulation occurs; in fact, continued dialysis is undesirable, since if all the electrolyte is removed the particles will lose their charge and coagulation will result.

The coagulating effect of electrolytes is a result of the electrical character of the colloidal particle. The sol is stable as long as the particles are able to repel one another, *i.e.* if they have a sufficiently high zeta potential. When an electrolyte is added, the ions of opposite sign to the particles will tend to be adsorbed on the surface, thus reducing the net charge on the particle. The higher ionic concentration also causes the double layer to contract in width. Both these factors reduce the value of the zeta potential, until the repulsion between particles is no longer great enough to prevent coagulation. Ions with a

multiple charge will be more effective in reducing the potential, so that the concentration necessary to bring about coagulation will be less.

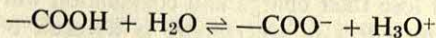
17.6. Lyophilic sols

These consist of solutions of substances of very high relative molecular mass (from several thousand up to a few millions), and the dissolved material is said to be *lyophilic* (solvent loving) to distinguish it from the lyophobic particles in a sol, which are insoluble in the dispersion medium. Very large molecules are usually polymers, *i.e.* they have been built up from a large number of small units all of the same type. Examples of naturally-occurring polymers are starch and cellulose (with glucose units), and proteins (from amino acids), while there are very many types of man-made polymers, *e.g.* polyethene, polystyrene, nylon, etc.

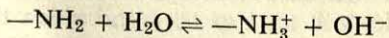
Lyophilic colloidal solutions can be made by dissolving the material in a suitable solvent. Substances of high relative molecular mass do not dissolve very readily, and frequently the solid tends to absorb the solvent, causing swelling, *e.g.* gelatin swells in cold water, and rubber in benzene. Such substances dissolve more readily on heating. The particles in this type of colloid are single molecules, which are usually solvated, *i.e.* covered with a layer of adsorbed solvent molecules that is probably one molecule thick. The molecular size is often near the lower end of the colloidal range, so that their light-scattering power may be small and the Tyndall effect much weaker than is the case with lyophobic sols.

One striking difference between lyophilic and lyophobic systems is in their electrical properties. Electrophoresis experiments show that the charge on lyophilic molecules in solution may be small, or even zero, without greatly affecting the stability of the system. This shows that the stability does not depend on the zeta potential (as with lyophobic particles). It is, in fact, due to the solvated layer. As a result, moderate concentrations of electrolytes do not cause precipitation. Very high electrolyte concentrations will give precipitation, probably by removing the solvated layer: this is known as the "salting-out" effect.

The charge on large molecules is frequently due to ionisation of certain acidic or basic groups, as in the case of proteins, which contain both the carboxylic acid group —COOH and the basic amino group —NH_2 . In acid solution the ionisation of the acid groups



is suppressed by the high concentration of hydrogen ions, while the ionisation of the basic groups



is increased, so that the molecule has a net positive charge. In an alkaline solution, on the other hand, the acidic groups are ionised more than the basic groups and the charge is negative. At a certain definite

pH the acidic and basic groups ionise to the same extent, and the molecule is uncharged. This is known as the *isoelectric point*, and can be demonstrated by observing the electrophoretic motion of the molecules in solutions of different pH. The speed and direction of travel vary with the pH, and at the isoelectric point there is no movement at all.

If a lyophilic substance is added to a lyophobic sol, the latter becomes much more stable in the presence of electrolytes. This is known as "protection" of the sol. It is probable that a complete layer of lyophilic molecules is formed round each sol particle, thus making it more lyophilic in nature and therefore less sensitive to added electrolytes. Gelatin is an example of a colloid with good protective action.

17.7. Association colloids

A solution of a soap (the salt of a fatty acid) is an example of an electrolytic solution that has colloidal properties. The apparent relative molecular mass of a soap, as measured by osmotic pressure or freezing point depression, is found to be much greater than expected, thus showing that the molecules are associated into aggregates of considerable size. At the same time, the solution has the high electrical conductance that would be expected from an ionic solute. These experimental facts can be accounted for in the following way. On dissolving a soap, e.g. sodium palmitate ($C_{15}H_{31}COONa$), the negative ions associate to form an ionic *micelle* which is of colloidal size (Fig. 108). The hydrocarbon portion of the ion is inside the micelle, and the ionised groups at the surface. Both the micelle and the positive ions are free to move in an electric field and the solution will therefore have a high conductance.

Molecules which exhibit this type of behaviour have a large hydrocarbon portion and an end-group which either is already ionised, or can ionise in water (e.g. acidic or basic groups). In addition to soaps, this includes the synthetic detergents, many of which are the salts of either organic sulphonic acids or organic bases. The action of a *detergent* is

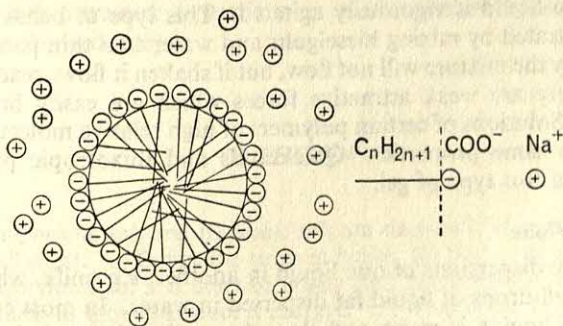


Fig. 108. A micelle in a soap solution

to remove dirt from a surface, and since the dirt is usually held on the surface by oil or grease it is the removal of the latter that is the real problem. Molecules of the type described, when dissolved in water, enable the water to "wet" the surface to be cleaned more effectively, so that the grease and dirt is pushed off. This is not sufficient, however; the detergent solution must also carry off the grease. This is brought about by the grease particles either being absorbed into the micelles (*solubilisation*), or being emulsified (*see below*).

17.8. Gels

Sols that have a fairly high concentration of dispersed solid sometimes change spontaneously into a semi-solid form known as a *gel*. An example may be seen in the behaviour of gelatin, which dissolves in warm water to form a colloidal solution but, when the latter is cooled, sets to a jelly. Gels are formed by the interlocking of the dispersed particles, making a rather loose framework inside which the liquid dispersion medium is contained. The strength of the framework will depend on the nature of the links that hold it together, so that gels vary widely in rigidity, from the jelly type which is only semi-solid up to gels which are quite rigid (*e.g.* silica gel). It is possible, however, to distinguish three main types, on the basis of their mechanical properties.

Elastic gels. Jellies are classed as elastic gels because they have the property of elasticity, *i.e.* their shape can be altered by applying a small force, but on removing the force they return to their original shape. Gelatin, starch and soaps are examples of substances that form elastic gels. The linkages between the molecules are due to electrical attraction between the ionised or polar groups.

Rigid gels. When an acid is added to a solution of sodium silicate, the molecules of silicic acid that are produced immediately polymerise, and silica gel is formed. The gel has a network linked by chemical bonds, which gives it a strong and rigid framework. Gels of this type are known as rigid gels.

Thixotropic gels have the property of being semi-solid when at rest, but become liquid if vigorously agitated. This type of behaviour can be demonstrated by mixing kieselguhr and water to a thin paste: when tilted slowly the mixture will not flow, but if shaken it flows readily. The linkages here are weak attractive forces which are easily broken by agitation. Solutions of certain polymers of high relative molecular mass exhibit the same properties. Quicksands and thixotropic paints are examples of this type of gel.

17.9. Emulsions

These are dispersions of one liquid in another, *e.g.* milk, which consists of small drops of liquid fat dispersed in water. In most emulsions one of the liquids is water and the other a liquid that is immiscible with water, such as an oil or fat. Either liquid can constitute the dis-

perse phase, so that emulsions are classified as belonging to either the *oil in water* or the *water in oil* type. Emulsions cannot be formed spontaneously by dispersing one of the liquids into small drops, but require the presence of an *emulsifying agent* to stabilise the droplets. This can be shown by shaking up an oil with water: the oil breaks up readily into droplets, but when the mixture is left to stand the drops coalesce until the two liquids have separated completely. If, however, a small quantity of soap or synthetic detergent is added to the water, then on shaking a stable emulsion will be formed. The emulsifying agent is adsorbed at the surface between the two liquids, forming a layer around the droplets of the dispersed liquid which gives them their stability. This example also illustrates the way in which detergents can carry away oil and grease in the washing water, in the form of an emulsion.

Emulsions are usually opaque, owing to the difference in refractive index between the two liquids. The particles tend to be larger than those in sols, and are at the upper end of the colloidal size range. A certain number of larger particles are frequently present in an emulsion, and if it is of the oil in water type they will tend to rise to the top since they are lighter than the water. This is termed *creaming*, and occurs in milk. The large particles can be broken up by the process of *homogenisation*, in which the emulsion is forced, under pressure, through a narrow gap. Very concentrated emulsions can be made, with as much as 90% of the volume occupied by the disperse phase; by comparison, a lyophobic sol is very dilute (usually less than 1%).

The droplets in an emulsion are often negatively charged, but their stability is due to the film of emulsifying agent surrounding them rather than to their electrical properties. As a result, emulsions are difficult to break. When they have to be broken, as is often necessary in industrial processes, the methods used include centrifuging (based on the difference in density between the two liquids); destroying or neutralising the emulsifying agent; and the Cottrell method, in which the emulsion is passed between electrodes charged to a very high voltage, when the droplets are attracted towards one of the electrodes (usually the positively charged one).

QUESTIONS

G.C.E.

1. Both *lyophilic sols* and *lyophobic sols* are electrically charged and show the Tyndall effect. (a) Define the terms in italics. (b) Name one lyophilic sol and one lyophobic sol and describe briefly their preparations. (c) Describe an experiment to show that a sol is charged. (d) What is the Tyndall effect? Describe an experiment to demonstrate it. [A.E.B., 1975]

2. Describe THREE different methods by which you would prepare colloidal

solutions, illustrating your answer by reference to ONE particular example for each method. What are the properties of colloidal solutions which distinguish them from true solutions? Give an account of the precipitation of colloidal particles by electrolytes.

[Oxford]

3. Describe how you would prepare colloidal solutions of (a) a metal, (b) arsenic trisulphide, (c) a hydroxide free from electrolytes. What is the Brownian movement and how is it explained? What do you understand by the term *electrophoresis* (cataphoresis) and how would you demonstrate this phenomenon?

[Oxford, "S"]

4. Explain the terms (i) dialysis, (ii) reversible colloid, (iii) peptisation (iv) disperse phase. Give one example of each term. What would you expect to see happen when a colloidal solution of silver is treated as follows: (v) a beam of light is passed through it, (vi) an electrolyte is added to it?

[London]

5. What properties characterise a colloidal solution? A colloidal solution of mercury contains 0.10 g of mercury per dm^3 , and a count shows 10^9 colloidal particles in each cm^3 of solution. Calculate the average number of mercury atoms in each colloidal particle. [Take the relative atomic mass of mercury as 200 and the Avogadro constant as 6×10^{23} .]

[Cambridge, "S"]

APPENDIX I

SI UNITS

The abbreviation SI stands for *Système International d'Unités*, which is a system of units based on the metric system and approved by the international authority on units (CGPM). The names and symbols for the basic SI units are as follows:

<i>Physical quantity</i>	<i>Name of SI unit</i>	<i>Symbol for SI unit</i>
length	metre	m
mass	kilogram	kg
time	second	s
electric current	ampere	A
thermodynamic temperature	kelvin	K
amount of substance	mole	mol
luminous intensity	candela	cd

Temperature

The kelvin is used to denote both the temperature on the thermodynamic scale, and also a temperature interval: thus heat capacity is in the units of J K^{-1} (energy per degree). The value of the kelvin is fixed by defining the temperature of the triple point of water as 273.16 K (this makes the ice point 273.15 K).

The degree Celsius ($^{\circ}\text{C}$) is not an SI unit, but will probably continue to be used for many temperature measurements. As a temperature interval, it is identical to the kelvin. As a measure of temperature, it indicates the temperature above the ice point (which is therefore 0°C). It thus follows that:

$$\text{thermodynamic temperature} = \text{Celsius temperature} + 273.15$$

The mole

The amount of a substance is measured in terms of the number of elementary particles, or units, that are present. The elementary unit may be a molecule, an atom, an ion, an electron, *etc.* The mole is the amount of substance that contains the same number of elementary units as there are atoms in 0.012 kg of carbon-12.

Derived SI units with special names

For physical quantities other than the basic ones, the SI units are arrived at by suitable combination of the basic units. In the case of some of these derived units, special SI names and symbols have been adopted. The following list includes only those used in this book:

<i>Physical quantity</i>	<i>Name of SI unit</i>	<i>Symbol for SI unit</i>	<i>Definition of SI unit</i>
frequency	hertz	Hz	s^{-1}
energy	joule	J	$kg\ m^2\ s^{-2} = N\ m$
force	newton	N	$kg\ m\ s^{-2} = J\ m^{-1}$
pressure	pascal	Pa	$kg\ m^{-1}\ s^{-2} = N\ m^{-2}$
electric charge	coulomb	C	$A\ s$
electric resistance	ohm	Ω	$kg\ m^2\ s^{-3}\ A^{-2} = V\ A^{-1}$
electric conductance	siemens	S	$kg^{-1}\ m^{-2}\ s^3\ A^2 = \Omega^{-1}$
electric potential difference	volt	V	$kg\ m^2\ s^{-3}\ A^{-1} = J\ A^{-1}\ s^{-1}$

Fractions and multiples of units

Fractions or multiples of either the basic SI units, or the derived SI units with special names, are obtained by the use of the usual prefixes. Those used in this book are as follows:

	<i>Prefix</i>	<i>Symbol</i>
10^3	kilo	k
10^{-1}	deci	d
10^{-2}	centi	c
10^{-3}	milli	m
10^{-6}	micro	μ
10^{-9}	nano	n
10^{-12}	pico	p

Note that, in the case of units of mass, the prefix is to be put in front of the symbol for gram (g). Thus $1\ g = 10^{-3}\ kg$; $1\ mg = 10^{-6}\ kg$.

Volume

The SI unit of volume is the cubic metre (m^3). For many purposes the most convenient fraction is the cubic centimetre ($cm^3 = 10^{-6}\ m^3$). The litre is not an SI unit, but has been redefined as being equal to a cubic decimetre ($dm^3 = 10^{-3}\ m^3$). There is little point in retaining the old term, and the unit dm^3 is used in this book. Thus molar concentrations become $mol\ dm^{-3}$.

Pressure

The SI unit of pressure (which is equal to force per unit area) is the pascal, symbol Pa ($= N\ m^{-2}$). The old units of atmospheres or millimetres of mercury are related to the SI units as follows:

$$1\ atm = 760\ mm\ Hg = 101\ 325\ Pa$$

A convenient unit for normal pressures is kilopascals (kPa), giving around 100 kPa for normal atmospheric pressures. For converting pressures given in mm Hg to SI units, the following equation is useful:

$$1\ mm\ Hg = 133\ Pa$$

APPENDIX II

ANSWERS TO QUESTIONS

Chapter 2

- Use of the mass spectrometer, §2.7. Standard for relative atomic mass, §1.4. Isotopes, §2.5. The element contains a radioactive isotope which is an α -emitter.
- (a) Proton (1, +1), neutron (1, 0), electron (1/1800, -1).
(b) §2.2.
(c) (i) ${}_{11}^{24}\text{Na} \rightarrow {}_{12}^{24}\text{Mg} + {}_{-1}^0\text{e}$
(ii) ${}_{7}^{14}\text{N} + {}_0^1\text{n} \rightarrow {}_6^{14}\text{C} + {}_1^1\text{H}$
(iii) ${}_{14}^{27}\text{Si} \rightarrow {}_{13}^{27}\text{Al} + {}_{+1}^0\text{e}$
(iv) ${}_{5}^{10}\text{B} + {}_2^4\text{He} \rightarrow {}_7^{13}\text{N} + {}_0^1\text{n}$
(e) Prepare, at the same temperature, saturated solutions of the radioactive lead(II) chloride and also of normal lead(II) chloride. Filter off the solutions, and to the radioactive solution add some normal lead(II) chloride: after a time, the solid will be found to be radioactive. Similarly, on adding radioactive solid to the inactive solution, the latter will be found to acquire radioactivity. This demonstrates that in the equilibrium $\text{PbCl}_2(\text{s}) \rightleftharpoons \text{Pb}^{2+}(\text{aq}) + 2\text{Cl}^{-}(\text{aq})$ both forward and reverse processes are still taking place.
- (a) p. 14. (b) p. 13.
(c) (i) ${}_{13}^{27}\text{Al} + {}_1^1\text{H} \rightarrow {}_{12}^{24}\text{Mg} + {}_2^4\text{He}$
(ii) ${}_{16}^{32}\text{S} + {}_0^1\text{n} \rightarrow {}_{15}^{32}\text{P} + {}_1^1\text{H}$
- (a) Emissions, §2.2. Numbers before symbols, §2.5.

$$P = {}_{90}^{230}\text{Th}; Q = {}_{93}^{239}\text{Np}; R = {}_{91}^{235}\text{Pa}; S = {}_1^1\text{H}. (b) X = {}_{-1}^0\text{e}.$$

- Statements 1 and 3 are correct.

Chapter 3

- Electrovalence, §3.2; covalence, §3.3. Tetra-ammonium cupric ion and $\text{NH}_3 \cdot \text{BF}_3$, p. 38.
- (a) §1.4. (b) §2.3. (c) §2.5.
- (a) p. 39(d). (b) Lithium hydride is Li^+H^- (see table of electronegativities, §3.4. (c) p. 32. (d) Reactivity increases with greater ease of loss of the valence electron to form a positive ion (i.e. lower ionisation energy). The latter decreases as the valence electron is situated in a shell further from the nucleus (see p. 21). (e) The

boron accepts two electrons from the fluorine atom (*see* p. 38), thus weakening the H—F bond.

5. (a) p. 36. (b) §7.3. (c) Ionic. (d) *See* p. 38 for a similar complex ion. (e) *See* illustration on p. 120.
6. Definition of molecule, §3.1. (a) Hydrogen-bonding between molecules, §3.7. (b) p. 38. (c) Covalent three-dimensional structure similar to diamond, §7.3. (d) §7.3, *Compounds*. (e) Probably $[\text{Ni}(\text{H}_2\text{O})_6]^{2+} \text{SO}_4^{2-}$ with the other water molecule hydrogen-bonded.

Chapter 5

1. (a) Charles's law, §5.1; kinetic interpretation, §5.5. (b) pV decreases with increasing pressure. *See* §5.6. (c) §12.3 and Fig. 18.
2. (a) (i) p. 50. (ii) §5.4. (b) (i) $1.22 \times 10^5 \text{ Nm}^{-2}$. [$\text{Nm}^{-2} = \text{Pa}$.] The iodine molecules are 40% dissociated.
3. B.
4. §5.5. (i) 3.99 kJ (*see* p. 70). (ii) 250 m s^{-1} . (iii) 2.00. (iv) 120 s. (v) §5.4; 120 s.
5. Ideal gas, §§5.2 and 5.5. Real gas deviations, §5.6. (a) p. 64. (b) §12.3 and Fig. 18. Root mean square velocity of oxygen molecules = 480 m s^{-1} .
6. §5.5. Van der Waals' equation, §5.6. Rate of diffusion, p. 64. Ammonium chloride will form 0.59 m from the ammonia end of the tube.
7. (a) §5.5. (b) (ii) Fig. 20 and p. 68. (c) §5.8. (d) The observations show that, when ozone decomposes, the volume increases to one and a half times the original value. Hence, by Avogadro's law, $\text{O}_x = 1\frac{1}{2}\text{O}_2$, and $x = 3$.

Chapter 6

1. (a) §6.3. (c), (d) and (e), §6.4 and Fig. 34.

Chapter 7

1. §7.3 and pp. 53–4.
2. Definition, p. 101. Kinetic theory, §4.1. Melting point methods, pp. 102–3. Effect of impurity, p. 102.
3. (a), (b) and (c) §7.8. (d) Mercuric iodide is enantiomorphic (*see* §7.8), the red form being stable below 126°C . Diamond and graphite, Fig. 37.

Chapter 8

1. Definitions, §8.2. Determination, §8.3. Sodium sulphate, p. 113 and Fig. 49.

2. Transition point at 33°C (see p. 113 and Fig. 49).
3. See pp. 120–1.
4. Method, §8.8. Oxygen 33 % by volume.
5. C.
6. (a) §8.6. (b) p. 120. (c) 94 % (1.88 g).
7. Properties of metals, §3.6 and p. 96. Solid solution diagram, Fig. 54; practical details, §8.10 and Fig. 56 (cooling curve of type (a) but without the horizontal portion).
8. Close-packed lattice, p. 96. Metallic bond, §3.6. Eutectic diagram, Fig. 55, cooling curve Fig. 56, explanation §8.10.

Chapter 9

1. (a) Colligative properties, p. 134. (b) §9.5, §9.6, §9.7 or §9.9. (c) §9.11. (d) 364. (The Cd^{2+} and I^- ions are largely combined in the form of CdI^+ , CdI_2 , and CdI_3^-).
2. (a) §9.3. (b) Fig. 65. (c) Apparent molecular mass = 218 ($\text{C}_7\text{H}_6\text{O}_2$ = 122): partial (79 %) association into double molecules.
3. §9.6. Relative molecular mass = 124, indicating a molecule P_4 .
4. (a) 122. (b) $\text{C}_7\text{H}_6\text{O}_2$. (c) 244. (d) pp. 152 and 120.
5. 17 000.

Chapter 10

1. (a) (i) p. 134. (ii) 2.13 kN m^{-2} . (b) (ii) See Fig. 71. (iii) 85°C.
2. (a) §10.3. (b) See Fig. 74. (c) Raoult's law, §9.1. Positive deviation, §10.3. (d) Hydrogen bonds will be formed between water and ethanol molecules. (e) The distillate in (i) will be richer in ethanol, and in (ii) will be richer in water. § 10.3. (f) C_6H_6 and $\text{C}_6\text{H}_5\text{CH}_3$.
3. (a) (i) §6.4. (ii) §5.3. (b) §10.5. (c) (i) 98°C (from a plot of total vapour pressure against temperature). (ii) 30 % (find the vapour pressure of water at 98°C from the figures given, and subtract from 101.3 to obtain the vapour pressure of phenylamine).

Chapter 11

1. (a) (i) §11.5. (ii) §11.5. (b) (ii) $\Delta H_c^\circ = -1368.1 \text{ kJ mol}^{-1}$.
2. See §11.6 for determination of enthalpies of formation of organic compounds.
3. First law, §11.1. Enthalpy and internal energy, §11.2. Ethane, $\Delta H_f^\circ = -83 \text{ kJ mol}^{-1}$; ethene, $\Delta H_f^\circ = 43 \text{ kJ mol}^{-1}$.
4. (a) Fig. 38 (face-centred cubic). (b) Fig. 37. (i) -770 kJ mol^{-1} . (ii) -902 kJ mol^{-1} . Comment: see p. 181.

Chapter 12

1. (a) §12.5. (b) (i) Second order. (ii) First order. (c) 120 minutes.
2. Order of reaction, §12.5. (a) §12.3. (b) For plot of concentration of A_2 against time, *see* Fig. 81. (i) §12.3. (ii) Lowering the pressure will reduce the concentration. (iii) §16.1. (c) $k = 5.93 \times 10^{-4} \text{ s}^{-1}$, obtained by plotting $\log_{10} c$ against time (*see* p. 197).
3. Order, p. 192; molecularity, p. 186. (a) p. 193. (b) p. 197. The reaction is second order, $k = 8.1 \times 10^{-2} \text{ s}^{-1} \text{ mol}^{-1} \text{ dm}^3$, obtained by plotting $1/c$ against time (*see* §12.8).

Chapter 13

1. Dynamic equilibrium, §13.2. Pressure of zinc vapour = 0.236 atm.
2. Influence of pressure and temperature, §13.3.

$$(i) K_p = \frac{p_R^2 \times p_S}{p_P \times p_Q} \text{ Pa.} \quad (ii) K_c = \frac{[R]^2 [S]}{[P] [Q]} \text{ mol dm}^{-3}.$$

$$(iii) K_p = \frac{p_S}{p_P} \text{ (no units). } N_2O_4: (i) 0.153, (ii) 0.0958 \text{ Pa.}$$

$$3. (a) K_c = \frac{[SO_3]^2}{[SO_2]^2 [O_2]}. \quad (b) \text{mol}^{-1} \text{ dm}^3. \quad (c) K_p = \frac{p_{SO_3}^2}{p_{SO_2}^2 \times p_{O_2}} \text{ Pa}^{-1}$$

(d) §13.3. Addition of an inert gas reduces the partial pressures of all constituents.

4. Effect of temperature on reaction rate, §12.3. (a) and (b) §13.3. (c) $K_p = c(a + b + c)^2 / ab^2 P^2$. CO, 0.85 mol; H_2 , 1.70 mol; CH_3OH , 0.15 mol. $P = 15 \text{ 600 kPa}$.
5. C is correct.

Chapter 14

1. Definitions, §14.3. Determination of A_0 , p. 225. Ethanoic acid solution: $\alpha = 0.013$, $[H^+] = 0.0013 \text{ mol dm}^{-3}$. (a) Higher. (b) Lower. (c) Higher.
2. (a) §14.3. (b) §14.3. (c) (i) 0.013; (ii) 2.89. (d) Buffer solutions, §14.10.
3. (a) §14.8. (b) (i) 0.001 32; (ii) 1.76×10^{-5} . (c) HCl is the stronger acid.
4. (a) (i) 11; (ii) pH less than 11 (*see* p. 247). (b) Magnesium hydroxide will be precipitated, calcium hydroxide will not.
5. (a) §14.8. (b) §14.7. (c) Less than 7. (d) (i) 11.0; (ii) 2.7. (e) pH and strength of acids and bases, p. 236. (f) (i) p. 231; (ii) 1.78×10^{-5} (p. 239).
6. (a) Fig. 91. (b) §14.12. (c) (i) p. 230; (ii) p. 233.

7. Solubility product, §14.13. (a) $1.95 \times 10^{-6} \text{ mol}^3 \text{ dm}^{-9}$. (b) 0.0760 g dm^{-3} .

Chapter 15

1. (a) pp. 256 and 258. (b) (i) Ag^+ ; (ii) Cu^+ . (c) (i) p. 255; (ii) 1.10 V ; (iii) from left to right.
2. (i) 0.80 A ; (ii) 0.16 g .

Chapter 16

2. §16.1. (a) Manufacture of hydrogen from natural gas, §16.3; (b) Haber process for ammonia, §16.3; (c) contact process for sulphuric acid §16.3.
3. Iodine-propanone reaction, p. 277. (c) §12.3.
4. (a) p. 185. (b) p. 192. (i) Compare the surface area of silver as wire and as particles of colloidal size (see p. 286). (b) The manganese(II) ions produced by the reaction act as catalyst.

Chapter 17

1. (a) and (b) Lyophilic sols, §17.6; lyophobic sols, §17.2. (c) p. 291. (d) §17.4.
2. Preparation, §17.2. Properties, §17.4. Precipitation by electrolytes, §17.5.
3. (a) Dispersion method, §17.2; aggregation method, §17.2. (b) p. 289. (c) p. 288; purification, §17.3. Brownian movement, §17.4. Electrophoresis, p. 291.
4. (i) §17.3. (ii) Lyophilic sols are reversible because, if the solvent is completely removed, the solid can be redissolved to form a sol. (iii) p. 288. (iv) §17.1 and Table 14. (v) Tyndall effect, §17.4. (vi) coagulation, §17.5.
5. Properties, §17.4 and §17.6. 3×10^8 atoms per particle.

INDEX

- Absolute zero, 57
- Absorption coefficient, 122
- Abundance, isotopic, 10
- Acid, 229
 - degree of dissociation, 231
 - dibasic, 231
 - dissociation constant
 - determination, 233, 239
 - dissociation (ionisation) constant, 231
 - ionisation, 229
 - strong, 230
 - weak, 230
- Acid-base catalysis, 276-277
- Acid-base indicators, 240-241, 243-244
- Actinides, 25
- Activated complex, 188
- Activation energy, 188
- Adsorption, 281-284
- Air, liquefaction of, 87
- Allotropy, 104-106
- Alpha (α) particle, 6
- Aluminium chloride, 38, 222
- Alums, 98
- Ammonia, 33, 35, 46, 122, 208, 222, 229, 279
- Ammonium chloride, 79, 237
- Amorphous solids, 93
- Andrews, 83
 - isotherms, 84
- Anion, 221
- Anode, 220
- Arrhenius, 187
- Association, 44
 - colloids, 295
 - in vapour, 78
 - in solution, 151
- Aston, 9, 61
- Atomic
 - bomb, 14
 - energy levels, 19-22
 - number, 7
 - orbitals, 27
 - spectra, 18
 - theory, 2
- Atomic mass, relative, 3
 - by chemical methods, 15
 - by gas density, 17
 - by mass spectrometer, 15
 - variations, 17
- Atomicity of gases, 17, 71
- Avogadro constant, 47
- Avogadro's law, 57
- Azeotropic mixtures, 159-160
- Base, 229
 - degree of dissociation, 233
 - dissociation constant
 - measurement, 233
 - dissociation constants (table), 231
 - dissociation (ionisation) constant, 233
 - ionisation, 229
 - strong, 233
 - weak, 233
- Beckmann freezing point method, 143
- Beckmann thermometer, 140
- Becquerel, 6
- Benzene, 37, 46, 156
- Benzenecarboxylic acid, 120
- Berthollet, 2
- Berthollides, 2
- Berzelius, 4
- Beta (β) particle, 6
- Bimolecular reaction, 186
- Bohr atom, 19, 25
- Boiling point, 53-54, 89-90
 - diagram, 156
 - elevation, 136-138
 - elevation constants, 139
 - measurement, 91-92
 - mixtures, 156
 - variation with pressure, 90

- Bomb calorimeter, 171-172
- Bond
 - angle, 36
 - covalent, 33-37
 - dative (co-ordinate), 37-39
 - energy, 42-43, 179
 - hybrid, 36
 - hydrogen, 44
 - length, 41-42
 - metallic, 43
- Born-Haber cycle, 180-181
- Bosch process, 279
- Boyle, 1, 56
- Boyle's law, 56
- Bragg, 94
- Bredig, 288
- de Broglie, 26
- Brønsted and Lowry, 229
- Brownian movement, 51, 290
- Bubble-cap column, 158
- Buffer solution, 238
 - pH equation, 239
 - range, 239
- Bumping, 90
- Caesium chloride, 97, 98
- Calcium carbonate, 213, 215
- Calcium chloride, 32
- Calorimeter, 170-171
 - adiabatic, 171
 - bomb, 171-172
- Cannizzaro, 75
- Carbon, 13, 36, 99-100, 105-106
- Carbon dioxide, 46, 65, 73, 83, 84, 86, 97, 104, 122
- Catalysis
 - acid-base, 276-277
 - heterogeneous, 278-284
 - homogeneous, 276-278
- Catalyst, 274
 - acid-base, 277
 - fluidised bed, 279
 - Friedel-Crafts, 277-278
 - general characteristics, 274-276
 - metals and oxides, 279
 - poison, 283
- Cathode, 5, 220
- Cathode rays, 5
- Cathodic protection, 272
- Cation, 221
- Caustic soda, 233, 268
- Cell, chemical, 259-261
- Celsius degree, 299
- Chadwick, 8
- Characteristic temperature, 100
- Charles's law, 56
- Le Chatelier's principle, 101
- Chemical cell, 259-261
- Chemical equilibrium (*see also* Equilibrium), 201-218
- Chemical kinetics, 185-199
- Chemisorption, 282
- Chlorine, 33, 254, 269
- Colligative properties, 134
- Colloids, 286-287
 - association, 295
 - colloidal electrolyte, 295
 - emulsion, 296
 - gel, 296
 - lyophilic, 294
 - lyophobic, 287-294
- Common ion effect, 246
- Complex
 - intermediate, 188
 - ions, 38, 248
 - reaction, 186
- Condensation, 89
- Conduction of electricity
 - in electrolytes, 220-221
 - in metals, 220
- Conductivity
 - ionic, 226-227
 - limiting, 225
 - measurement, 223-224
 - molar, 224
 - strong and weak electrolytes, 224-225
- Conjugate acids and bases, 237
- Co-ordinate bond, 37-39
- Copper(II) sulphate hydrates, 215-216
- Corrosion of metals, 270
 - atmospheric oxidation, 270
 - electrolytic, 270-271
 - prevention, 271-272
- Cottrell boiling point method, 141
- Coulomb (unit), 264, 300
- Covalence, 30, 33-39
- Covalent compounds, properties of, 39
- Creaming of emulsions, 297
- Critical

- constants, 85
- pressure, 85
- solution temperature, 116
- temperature, 85
- Crookes, 5
- Crystal lattice, 94
- Crystal structure
 - elements, 95
 - ionic compounds, 97, 98
 - metals, 96
 - molecular compounds, 96–98
- Crystallisation, separation by, 115
- Crystals, 93
 - isomorphous, 98
 - x-ray diffraction by, 94
- Cubic lattice, 96
- Curie, Mme, 12
- Cyclopropane, 186
- Cyclotron, 13
- Dalton, 2, 4, 59
- Dalton's law of partial pressures, 59
- Daniell cell, 259–260
- Dative bond, 37–39
- Davisson and Germer, 26
- Debye (unit), 41
- Debye and Hückel, 224–225
- Debye, Scherrer and Hull, 94
- Decomposition potential, 262
- Degree of dissociation, 79
 - acid, 231
 - base, 233
- Degrees of freedom, 107
- Deliquescence, 216
- Detergent, 295
- Deuterium, 10, 14
- Dialysis, 289
- Diamond, 95
- Dicyanosilver ion, 38, 249
- Differential thermometer, 140
- Diffraction grating, 94
- Diffusion, 50
 - Graham's law of, 61
- Dilatometer, 191
- Dinitrogen
 - oxide, 191, 192
 - pentoxide, 187, 192
 - tetroxide, 79, 80, 212
- Dipole moment, 41
- Disappearing meniscus method, 85
- Disperse phase, 287
- Dispersion medium, 287
- Dissociation
 - of acids and bases, 229–233
 - constant, 231, 233
 - degree of, 79, 210–211, 213, 231, 233
 - of electrolytes, 152–153
 - energy, 42, 179
 - pressure, 214, 215–216
 - in vapour, 79
- Distillation, 156–163
 - azeotropic mixtures, 159
 - fractionation, 157–159
 - immiscible liquids, 161–163
 - reduced pressure, 160
- Distribution coefficient, 118
- Distribution law, 117
 - applications, 118–121
- DNA, 98
- Dry ice, 86, 104
- Dulong and Petit, 99
- Dumas vapour density method, 77
- Efflorescence, 215
- Einstein, 11, 18
- Electric double layer, 253
- Electrochemical series, 257
 - and chemical reactivity, 258–259
- Electrode
 - potential, 255–258
 - reactions, 252–255
 - reference standard, 255
 - sacrificial, 272
 - sign convention, 257
- Electrolysis, 220, 261–269
 - examples, 266–269
 - Faraday's laws, 264
 - measurement of transport number, 269
- Electrolytes, 221–223
 - colloidal, 295
 - conductivity, 223–228
 - strong and weak, 222
- Electrolytic
 - conduction, 220–221
 - corrosion, 270–271
- Electron, 6
 - affinity, 180
 - mass of, 6, 10
 - orbitals, 27
 - shells, 20, 21
 - wave nature of, 26

- Electronegativity, 40
- Electronic energy levels, 19–22
- Electronic
 - structure of atoms, 21–25
 - theory of valency, 30–31
- Electrophoresis, 291
- Electroplating, 267, 268, 272
- Electrovalence, 31–33
- Electrovalent compounds,
 - properties, 33
- Element, 1
 - tracer, 13
 - transitional, 24
 - transuranic, 13
- Emulsifying agent, 297
- Emulsions, 296–297
- Enantiotropy, 104
- Endothermic reactions, 166
- Energy
 - of activation, 188
 - changes, in reactions, 165–168
 - chemical, 165
 - of chemical bonds, 42–43, 179
 - from chemical cells, 260–261
 - conservation, law of, 165
 - of crystal lattice, 180
 - distribution, molecular, 54–55
 - of expansion, 69–70, 166
 - of hydration, 113
 - internal (intrinsic), 166
 - kinetic, 50
 - levels, atomic, 19–22
 - nuclear, 14
 - rotational, 50
 - units, 166
 - vibrational, 50
- Enthalpy, 168
 - of combustion, 169, 173
 - of formation, 173–177
 - of fusion, 49
 - of neutralisation, 242
 - of reaction, 168–169, 172–173, 177
 - of solution, 178–179
 - of vaporisation, 50
- Entropy, 182
 - changes, 182–183
- Equilibrium, chemical, 201–203
 - dynamic, 202
 - effect of catalyst, 205
 - effect of pressure, 204–205
 - effect of temperature, 204, 205
 - heterogeneous, 213–217
 - homogeneous, 206–213
- Equilibrium constant, 202
 - measurement, 217–218
- Equivalent mass, 16
- Esterification reaction, 11, 201, 211–212
- Ethanoic acid, 78, 230, 232, 276
- Ethanol, 90, 159, 160, 170, 281
- Ethene, 46
- Ethyl ethanoate, 190
- Eutectic
 - systems, 127–130
 - temperature, 127
- Evaporation, 88, 104
- Exothermic reaction, 166
- Faraday constant, 264
- Faraday's laws, 264
- First law of thermodynamics, 165
- First order reactions, 193–195
- Fluidised bed catalyst, 279
- Fractionating column, 158–159
- Fractionation, 157–158
- Free energy, 183
 - change, 183
- Freeze-drying, 104
- Freezing mixtures, 129
- Freezing point depression, 138–139
 - constants, 139
 - measurement, 143–145
- Friedel-Crafts catalyst, 277–278
- Fusion, enthalpy of, 49
- Galvanising, 272
- Gamma (γ) rays, 6
- Gas
 - constant, 58
 - density, 72–78
 - diffusion, 50, 61
 - equation, ideal, 58
 - heat capacity, 69–71
 - ideal, 61–62
 - kinetic theory, 61–64
 - liquefaction, 83–88
 - mixtures, 59–60
 - molar volume, 57, 68
 - molecular velocities, 64
 - non-ideal, 65–66
 - partial pressure, 59–60

- Gas laws
 Avogadro's, 57
 Boyle's, 56
 Charles's, 56
 Dalton's, 59
 Graham's, 61
Gay-Lussac, 57
Gay-Lussac's (Charles's) law, 56
Gels, 296
Giant molecule, 95
Goldstein, 6
Graham, 61, 289
Graham's law of diffusion, 61
Granulation of precipitates, 112
Graphite, 95
Guldberg and Waage, 202

Haber process, 279
Hahn and Strassmann, 13
Hampson, 87
Heat
 changes at constant pressure, 167
 changes at constant volume, 168
 of reaction, measurement,
 170-172
Heat capacity, 49
 of gases, 69-71
 of solids, 99-100
Henry's law, 121
Hertz (unit), 300
Hess's law, 174-177
Heterogeneous, 107
 catalysis, 276, 278-284
 equilibria, 213-217
HETP, of column, 159
Hexacyanoferrate(III) ion, 38
Hexagonal close-packed lattice, 96
Hittorf, 270
Homogeneous, 107
 catalysis, 276-278
 equilibria, 206-213
Homogenisation, 297
Hooker cell, 268
Hybrid bond, 36
Hydrated ions, 39, 248
Hydration
 energy, 113
 of ions, 39, 111, 222, 227, 248
Hydrochloric acid, 222, 229
Hydrogen, 15, 20, 33, 34, 65, 86,
 122, 217, 253, 255, 263, 279
Hydrogen bond, 44-45
 in association, 44, 78, 120, 152
 in solvation, 113
Hydrogen
 chloride, 33, 35, 41, 122, 160, 178,
 222, 229
 electrode, 253, 255
 iodide, 185, 186, 188, 192, 206
 ion, 39, 222, 227
 peroxide, 174-175
 sulphide, 247
Hydrogen ion concentration,
 acid solutions, 234-235
 base solutions, 235
 buffer solutions, 238-239
 during titration, 242
 measurement with indicators, 241
 salt solutions, 237
 water, 235
Hydrogenation, 275, 280
Hydrolysis of
 ester, 190, 193, 197, 276
 salts, 236-237
Hydronium ion, 39, 222

Ice, 44, 101
Ideal gas, 61-62
 equation, 58
Ideal solution, 134
Indicator, 240
 constant, 240
 range, 241
 use in titration, 242-244
Inhibition, 284
Interionic forces, 53
Intermolecular forces, 51-54
Internal energy, 166
Intrinsic energy, 166
Iodine, complex ion, 120
Ion, 31
 complex, 38-39, 248-249
 hydrated, 39, 222, 227, 248
Ion-pair, 153
Ionic
 atmosphere effect, 225
 conductivity, 226-227
 micelle, 295
 mobility, 227
 product of water, 234
 radius ratio, 98

- Ionisation, 221-222
 of acids, 229-230, 231
 of bases, 229-230
 constant, 231
 degree of, 231
 energy, 32, 180
 of water, 234
Isoelectric point, 295
Isomorphism, 98
Isopestic method, 135
Isotonic solutions, 147
Isotopes, 9
 abundance, 10
 applications, 11
 mass, 10-11
 radioactive, 12-14
Joule, 80, 165
Joule (unit), 166, 300
Joule-Thomson effect, 80, 86
Kellner-Solvay cell, 268
Kelvin (unit), 56, 299
Kinetic energy of molecules, 50
Kinetic theory of
 gases, 61-64
 matter, 49-55
Kinetics, chemical, 185-199
Kirchhoff equation, 178
Kohlrausch, 226
Lanthanides, 25
Lattice energy, 113, 180
Laue, 94
Law of
 conservation of energy, 165
 conservation of mass, 2
 constant composition, 2
 mass action, 202
 multiple proportions, 2
 partial pressures, 59
 reaction rate, 185
 reciprocal proportions, 3
Layer lattice, 95
Lewis, 30
Ligand, 248
Limiting density, 73
Linde, 87
Liquids, 88
 boiling point, 89-92
 partial miscibility, 116-117
 superheating, 90
 vapour pressure, 88-89, 90
Liquefaction of gases,
 conditions for, 83-86
 methods, 86-88
Lithium, 43-44
Litmus, 241, 243
Low temperatures, 86
Lyophilic sols, 294
Lyophobic sols, 287
 coagulation, 292-294
 electrical properties, 291-292
 optical properties, 290
 preparation, 287-289
 protection, 295
 purification, 289
Magnesium oxide, 32
Mass action, law of, 202
Mass
 defect, 11
 number, 10
 spectrograph, 9-11
 spectrometer, 15
Mass-energy relationship, 11
Maxwell, 54
Melting point, 53, 54, 100-101
 measurement, 102-103
 variation with pressure, 101
Mendeleef, 17
Metals,
 atmospheric oxidation, 270
 catalysts, 279
 crystal structure, 96
 electrical conduction, 220
 electrolytic corrosion, 270-271
 electroplating, 267
 protection, 271-272
Metallic bond, 43
Metastable equilibrium, 105
Methane, 33, 46, 86, 179
Methanol, 117, 276, 281
Methyl
 orange, 240, 241, 243, 244
 red, 241, 243
Micelle, 295
Microbalance, gas density, 74
Millikan, 6
Miscibility of liquids, 116-117
Mixed crystals, 99
Molality, 112

- Molar concentration (units), 300
Molar conductivity, 224
 limiting value, 225
Molar volume of gas, 57, 68
Mole, 47, 299
Mole fraction, 60, 133
Molecule, 30
Molecular
 collision rate, 187
 orbital, 34
 structure, 45-46
 velocity, 64
Molecular mass, abnormal, 151-153
Molecular mass, relative, 47
Molecular mass determination by
 boiling point elevation, 141-142
 freezing point depression, 143-145
 gas density, 73-75
 gaseous diffusion, 61
 osmotic pressure, 150-151
 vapour density, 75-78
 vapour pressure lowering, 135-136
Monotropy, 105
Moseley, 7

Nernst, 117, 256
Nernst equation, 256
Neutralisation, 242-244
 curves, 243
 enthalpy of, 242
 pH changes during, 242
Neutrino, 12
Neutron, 8
 mass of, 10
Newton (unit), 300
Nitrogen, 66, 86, 122
Nitrogen oxide, 274
Non-ideal behaviour,
 gases, 65-68
 solutions, 151-153
Nuclear
 energy, 14
 fission, 13-14
 fusion, 14
 reactor, 14
 transmutations, 11-13
Nucleus, 7
 constitution, 8, 10

Octet rule, 30
Ohm (unit), 300

Optical activity, 191
Orbitals
 atomic, 27
 molecular, 34
Order of reaction, 192
 determination, 197
Osmometer, 149
Osmosis, 145-147
 in living organisms, 147
Osmotic pressure, 147-148
 measurement, 149-150
Ostwald, 112
Overgrowth, in crystals, 99
Overperfect behaviour, gas, 65, 68
Overpotential, 263
Oxidation
 in electrolysis, 262
 in ionic solutions, 254-255,
 258-259
 of metals, 270-272
Oxygen, 36, 65, 86, 122, 263

Partial pressure, gas, 59-60
Partially miscible liquids, 116-117
Partition coefficient, 118
Pascal (unit), 300
Peptisation, 288
Periodic table, 23
 explanation, 17-18, 22-25
Petroleum cracking, 280
Pfeffer, 147
pH, 235
 of acid and base solutions, 236
 of buffer solutions, 239
 during neutralisation, 242-244
 neutral, 235
 of salt solutions, 237
Phase, 107
 diagram, 107
 rule, 108
Phenolphthalein, 240, 241, 243, 244
Phenylamine, 160, 162
Phosphorus, allotropy, 106
Phosphorus pentachloride, 79, 210
Photochemical reactions, 198
Photography, 199
Photosynthesis, 198
Physical adsorption, 282
Pi (π) bond, 36-37
Planck, 18, 198
Planck's quantum equation, 19

- Plasmolysis, 147
- Polar
 - bond, 40
 - molecules, 45-46
- Polymers, molecular mass
 - determination, 151
- Polymerisation, 278
- Polymorphism, 104
- Positive rays, 6
- Potassium
 - chlorate, 114
 - chloride, 130, 152, 225
- Powder camera, 94
- Precipitation of sparingly soluble salts, 246-248
- Pressure, critical, 85
- Pressure, vapour; *see* Vapour pressure
- Propanone, 277
- Proton, 6
 - charge, 6
 - mass, 10
 - number, 7
- Proton transfer theory, 229-230
- Quantum
 - numbers, 20
 - theory, 18-19
- Radiation, 6
- Radioactive
 - decay, 11-12
 - half-life, 11-12, 195
 - tracers, 13
- Radioactivity, 6-7, 11-13
- Radiocarbon dating, 13
- Raoult's law, 134
- Rast freezing point method, 145
- Rate constant, 185
- Rate equations,
 - first order, 194
 - second order, 196
- Rate of molecular collisions, 187
- Rays, α -, β - and γ -, 6
- Reaction,
 - bimolecular, 186
 - complex, 186
 - effect of temperature on rate, 187-189
 - first order, 192, 193-195
 - measurement of rate, 189-192
 - order, 192
 - photochemical, 198
 - rate law, 185
 - reversible, 201
 - second order, 192, 195-197
 - thermal, 198
 - unimolecular, 186
- Recrystallisation, 115-116
- Reduction
 - in electrolysis, 262
 - in ionic reactions, 254-255, 258
- Reflux, 158
- Refrigerator liquids, 86
- Regnault gas density method, 73
- Relative atomic mass, 3
- Relative molecular mass, 47
- Reversible reaction, 201
- Röntgen, 7
- Rotational energy, 50
- Rutherford, 6, 7, 8, 12, 25
- SI units, 299-300
- Sacrificial electrode, 272
- Salt
 - hydrolysis, 236-237
 - bridge, 255
- Salting-out effect, 294
- Schrödinger, 26
- Schulze-Hardy, rule, 293
- Scientific method, 1
- Second
 - law of thermodynamics, 182
 - order reactions, 195-197
- Seeding, 112
- Semi-permeable membrane, 146
- Sherardising, 272
- Sidgwick, 30
- Siemens (unit), 300
- Sigma (σ) bond, 36
- Silver chloride, 245
- Siwoloboff boiling point method, 91, 92
- Sodium
 - ethanoate, 237
 - carbonate, 216
 - chloride, 31, 97, 98, 111, 114, 180
 - hydroxide, 233, 266-267, 268
 - sulphate, 113-114
- Solids, 93
 - allotropy, 104-106
 - concentration, 214

- crystal structure, 94–99
- heat capacity, 99
- melting point, 101–103
- sublimation, 104
- triple point, 100–101
- vapour pressure, 100
- Solid solution, 99, 125–127
- Sols, 287, *see also* Lyophilic sols, Lyophobic sols
- Solubility, 110–111
 - gases, 121–125
 - liquids, 116
 - solids, 111–115
 - of sparingly soluble salts, 244–246
- Solubility product, 245
 - in analysis, 246–248
- Solution,
 - colloidal, 294
 - enthalpy of, 178–179
 - ideal, 134
 - isotonic, 147
 - non-ideal, 151–153
 - saturated, 111, 112
 - supersaturated, 112
 - vapour pressure of, 133–135
- Solvation, 111, 113
- Solvent extraction, 118–120
- Space lattice, 95
- Sparingly soluble salts, 244–248
- Spectrum, 18
 - atomic, 18–19
 - infrared, 71
- Spontaneous reaction, 181–183
- Standard
 - electrode potential, 256, 257
 - enthalpy of formation, 174
 - hydrogen electrode, 255
 - temperature and pressure, 57
- Stas, 16
- States of matter, 49
 - gas, 56–80
 - liquid, 88–92
 - solid, 93–106
- Steam distillation, 162–163
- Styrene, 280
- Sublimation, 104
- Sucrose, hydrolysis of, 191
- Sulphur, allotropy, 104–105
- Sulphuric acid, contact process, 280
- Supercooling, 143
- Superheating, 90, 141
- Surface tension, 88
- Suspension, 286
- Temperature,
 - Celsius, 299
 - characteristic, 100
 - critical, 85
 - eutectic, 127
 - kinetic explanation, 50, 63
 - thermodynamic, 56, 299
 - transition, 104
- Tetraamine copper (II) ion, 38
- Thermal
 - dissociation, 79
 - reaction, 198
- Thermochemical equations, 169
- Thermochemistry, 165–180
- Thermodynamic temperature, 56
- Thermodynamics,
 - first law, 166
 - second law, 182
- Thixotropic gel, 296
- Thomson, 5, 80
- Tinplating, 272
- Titration
 - acid-base, 242–243
 - of salts, 244
- Tracer isotopes, 13
- Transition temperature, 104
- Transitional elements, 24
- Transmutation, 11
- Transport number, 228–229, 269
- Transuranic elements, 13
- Triple point, 100, 101
- Turgid cell, 147
- Tyndall effect, 290
- Ultrafiltration, 290
- Ultramicroscope, 290
- Underperfect behaviour, gas, 65, 68
- Unimolecular reaction, 186
- Uranium, radioactive isotopes, 12
- Valency, 16, 30–31
- Van der Waals
 - equation, 68
 - forces, 51
- Van't Hoff
 - equation, 148
 - i* factor, 153
- Vaporisation, enthalpy of, 50

- Vapour, 49, 89
Vapour density, 75
 Dumas method, 77
 Victor Meyer method, 75
Vapour pressure, 89
 liquids, 88-89, 90
 mixtures of liquids, 155
 solids, 100
 solutions, 133-135
Velocity, molecular, 64
Vibrational energy, 50
Victor Meyer vapour density
 method, 75
Volt (unit), 300
Volume (unit), 300
Volumeter gas density method, 73
Water,
 acidic and basic properties, 230
 boiling point, 90
 ionisation, 234
 molecular structure, 33, 35, 45, 46
 triple point, 101
Water gas reaction, 217
Wave function, 26
Wave nature of electron, 26

x-rays, 7
 diffraction by crystals, 94

Zeta potential, 292



THE ENGLISH LANGUAGE BOOK SOCIETY, an association of leading British publishers, brings you essential, up-to-date textbooks at reduced prices.

The sterling price of PHYSICAL CHEMISTRY is

£2.40

Inside you will find a list of some other ELBS low-priced editions. Your local bookseller may also be able to show you a complete list of ELBS titles.

This logical and modern approach to the basic concepts of physical chemistry, has been written primarily for students studying for the General Certificate of Education at Advanced Level (including those taking Special papers), the National Certificate in Science (for which the appropriate sections of both Basic and Elective Chemistry are covered) and other examinations of comparable level outside Great Britain. To make sure that students can see how mathematical equations can be applied to specific problems there are many worked examples in the text. At chapter ends there are selected questions taken from actual papers set by leading examining bodies. This new Third Edition has been revised and now includes a new appendix containing answers to questions.